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THE RELATIVISTIC THEORY OF CHEMICAL BINDING

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Abstract

Starting from Breit's relativistic equation for a system of two electrons, it is shown that for a hydrogen molecule (or for a system of two electrons moving in a field of cylindrical symmetry) the component of the total angular momentum (J_z) along the axis of the molecule (axis of symmetry) is a constant of motion. Thus every eigenstate of the system is simultaneously an eigenstate of J_z also, and a state of the system will specify, besides its energy, only the eigenvalue of the component of the angular momentum parallel to the axis of symmetry. The form of the four large components of the wave function relating to their dependence on the azimuthal co-ordinates has been given.

The case of Russel-Saunders approximation has been considered in detail and the nature of the components of the wave function for the singlet and triplet states has been discussed. It is shown that the wave function for the ground state of the hydrogen molecule could be expressed as a sum of a set of symmetric functions of which the first term is the Heitler-London function, and that the wave function for a triplet state should be a superposition of anti-symmetric molecular orbitals. It is shown that relativistic theory brings about in a natural manner the facts relating to the ground state of the molecules C_2 and O_2. Finally, some remarks are made concerning the case of molecules for which the spin-orbit and the spin-spin couplings are strong.

I. Introduction

The theoretical solution of problems of molecular chemistry are based usually on one or the other of two methods, known as the Molecular Orbital Theory and the Valence Bond Theory.[1] In the former method, the binding electron is supposed to belong to the entire molecule and is assumed to be moving in the average potential field of the other electrons and the nuclei. The latter is the well-known theory of hydrogen molecule given by Heitler and London. An important consequence of this theory is that the ground state of the hydrogen molecule is the singlet state in which the spins of the two electrons are

opposite to each other and that the states with the spins parallel to each other are unstable. In both the above-mentioned methods, the spin of the electron is introduced as an independent extraneous factor in such a way as to comply with the requirements of the Pauli Exclusion Principle, but is not brought out as an integral part of the theory itself. In view of the very important role that the spin of the electron plays in the chemical binding in molecules, it is desirable to develop a theory based on a relativistic equation which will bring out the spin as an essential part of the mathematical formalism itself, and to analyse the consequences of such a theory. This, precisely, is the object of the present paper.

II. The Hamiltonian of a System of Two Electrons

Let us consider a system of two electrons interacting with each other. Let ϕ^{I}, $\mathbf{A}^{\mathrm{I}}$ and ϕ^{II}, $\mathbf{A}^{\mathrm{II}}$ denote respectively the scalar and vector potentials of electrons I and II disregarding their interaction. A relativistic wave equation for a system of two electrons interacting with each other and with an external electromagnetic field was given by Breit[2] in the year 1929.

The equation is

$$\left.\begin{aligned} &\Big\{p_0 + \sum_{k=1,2,3} (\alpha_k{}^{\mathrm{I}} p_k{}^{\mathrm{I}} + \alpha_k{}^{\mathrm{II}} p_k{}^{\mathrm{II}}) + (\alpha_4{}^{\mathrm{I}} + \alpha_4{}^{\mathrm{II}})\, mc \\ &\qquad + \frac{e^2}{2cr}\Big[\sum_k \alpha_k{}^{\mathrm{I}} \alpha_k{}^{\mathrm{II}} + \frac{(\boldsymbol{\alpha}^{\mathrm{I}} \cdot \mathbf{r})\,(\boldsymbol{\alpha}^{\mathrm{II}} \cdot \mathbf{r})}{r^2}\Big]\Big\} \end{aligned}\right\} \psi = 0 \qquad (1)$$

where

$$p_k{}^{\mathrm{I}} = -i\hbar \frac{\partial}{\partial x_k{}^{\mathrm{I}}} + \left(\frac{e}{c}\right) \mathrm{A}_k{}^{\mathrm{I}};$$

$$p_k{}^{\mathrm{II}} = -i\hbar \frac{\partial}{\partial x_k{}^{\mathrm{II}}} + \left(\frac{e}{c}\right) \mathrm{A}_k{}^{\mathrm{II}}$$

and

$$p_0 = \frac{i\hbar}{c} \frac{\partial}{\partial t} + \frac{e}{c}(\phi^{\mathrm{I}} + \phi^{\mathrm{II}}) - \frac{e^2}{cr} \qquad (2)$$

The matrices $\alpha_k{}^{\mathrm{I}}$ and $\alpha_k{}^{\mathrm{II}}$ are the usual Dirac matrices, but now they operate on the first and second suffixes respectively. The representations that we choose for these are given in Appendix I. The wave function ψ has sixteen components which will be designated by ψ_{mn} ($m, n = 1, 2, 3, 4$), the first

suffix m referring to electron I and the second suffix n referring to electron II. If a^{I} and b^{II} be any of the above-mentioned matrices, then

$$(a^{\mathrm{I}}b^{\mathrm{II}}\psi)_{m,n} = \sum_{k,l} a_{mk}{}^{\mathrm{I}} b_{nl}{}^{\mathrm{II}} \psi_{kl} \tag{3}$$

Equation (1) is thus equivalent to sixteen differential equations in the sixteen functions ψ_{mn}.

By writing in (1)

$$\alpha_1 = \rho_1\sigma_1; \qquad \alpha_2 = \rho_1\sigma_2; \qquad \alpha_3 = \rho_1\sigma_3 \tag{4}$$

where ρ_1, σ_1, σ_2, σ_3 are the matrices (4) of Appendix I, we see that the Hamiltonian of the system is given by

$$\begin{aligned} \mathrm{H} = {} & e(\phi^{\mathrm{I}} + \phi^{\mathrm{II}}) + \frac{e^2}{r} - \rho_1{}^{\mathrm{I}} c\,(\boldsymbol{\sigma}^{\mathrm{I}} \cdot \mathbf{p}^{\mathrm{I}}) \\ & - \rho_1{}^{\mathrm{II}} c\,(\boldsymbol{\sigma}^{\mathrm{II}} \cdot \mathbf{p}^{\mathrm{II}}) - mc^2(\alpha_4{}^{\mathrm{I}} + \alpha_4{}^{\mathrm{II}}) \\ & - \frac{e^2}{2r}\left[(\rho_1{}^{\mathrm{I}}\boldsymbol{\sigma}^{\mathrm{I}} \cdot \rho_1{}^{\mathrm{II}}\boldsymbol{\sigma}^{\mathrm{II}}) + \frac{(\rho_1{}^{\mathrm{I}}\boldsymbol{\sigma}^{\mathrm{I}} \cdot \mathbf{r})(\rho_1{}^{\mathrm{II}}\boldsymbol{\sigma}^{\mathrm{II}} \cdot \mathbf{r})}{r^2}\right] \end{aligned} \tag{5}$$

III. The x-Component of the Total Angular Momentum

We shall consider the case of the hydrogen molecule which is the simplest example of a two-electron molecular system. Let the origin be chosen at one of the nuclei and let the line of action of the molecule coincide with the positive direction of the x-axis. If the nuclei are denoted by the suffixes A and B, the potentials ϕ^{I} and ϕ^{II} are given by

$$\phi^{\mathrm{I}} = e\left(\frac{1}{r_{a_1}} + \frac{1}{r_{b_1}}\right)$$

and

$$\phi^{\mathrm{II}} = e\left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_2}}\right)$$

where $r_a = \sqrt{x^2 + y^2 + z^2}$ and $r_b = \sqrt{(x - \mathrm{R})^2 + y^2 + z^2}$, R being the internuclear distance.

Let $m_x{}^{\mathrm{I}}$ and $m_x{}^{\mathrm{II}}$ denote the x-component of the orbital angular momenta of electrons I and II respectively. Then the dynamical variable

$M_x = (m_x^{I} + m_x^{II})$ represents the x-component of the total orbital angular momentum of the system. In the same way, the quantity

$$S_x = \frac{\hbar}{2}(\sigma_x^{I} + \sigma_x^{II})$$

gives the component of the total spin angular momentum parallel to the axis of the molecule. The sum J_x of these two (*i.e.*)

$$J_x = m_x^{I} + m_x^{II} + \frac{\hbar}{2}(\sigma_x^{I} + \sigma_x^{II}) \tag{6}$$

represents therefore the x-component of the *total* angular momentum of the system parallel to the axis of the molecule.

It has been proved in Appendix II that

$$J_x H - H J_x = 0 \tag{7}$$

One can see from the Appendix that neither S_x nor M_x commutes with the Hamiltonian but only their sum has the property of commuting with H.

Thus the component of the total angular momentum parallel to the axis of the molecule is a constant of motion.

Since J_x commutes with H, every eigenfunction of H will be simultaneously an eigenfunction of J_x also. An eigenstate, thus, is specified by two parameters, namely, the energy of the state and the eigenvalue of the component of the total angular momentum parallel to the axis of the molecule.

IV. THE EIGEN ψ'S OF J_x

Let us denote the eigenvalues of J_x by $M\hbar$ where M is yet undetermined. The equation

$$J_x\psi = M\hbar\psi \tag{8 a}$$

or

$$\left[m_x^{I} + m_x^{II} + \frac{\hbar}{2}(\sigma_x^{II} + \sigma_x^{II})\right]\psi = M\hbar\psi \tag{8 b}$$

will then be equivalent to sixteen equations in the sixteen components of ψ. We write here only four of these equations, namely, those involving the four large components ψ_{33}, ψ_{34}, ψ_{43} and ψ_{44} of ψ. From (3), it follows that the (3, 3), (3, 4), (4, 3) and (4, 4)th components of the equation (8) are given by

$$-i\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)\psi_{33}=(\mathrm{M}-1)\,\psi_{33}$$

$$-i\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)\psi_{34}=\mathrm{M}\psi_{34}$$

$$-i\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)\psi_{43}=\mathrm{M}\psi_{43}$$

$$-i\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)\psi_{44}=(\mathrm{M}+1)\,\psi_{44} \qquad (9)$$

Hence

$$\psi_{33}=f_{33}(r_1, r_2, \theta_1, \theta_2)\, e^{i(\overline{m_1-1}\phi_1+m_2\phi_2)}$$

$$\psi_{34}=f_{34}(r_1, r_2, \theta_1, \theta_2)\, e^{i(m_1\phi_1+m_2\phi_2)}$$

$$\psi_{43}=f_{43}(r_1, r_2, \theta_1, \theta_2)\, e^{i(m_1\phi_1+m_2\phi_2)}$$

$$\psi_{44}=f_{44}(r_1, r_2, \theta_1, \theta_2)\, e^{i(m_1\phi_1+\overline{m_2+1}\phi_2)} \qquad (10)$$

where $m_1 + m_2 = \mathrm{M}$.

Since the ψ's should be single-valued, the numbers m_1 and m_2 are integers.

One can verify that the other twelve small components satisfy differential equations of the type (9) and their form is therefore similar to the expressions given by (10).

Now it has been shown by Breit[2, 3] that equation (1) involving sixteen components can be reduced to an approximate equation with four components expressed in terms of Pauli's spin matrices. This reduced equation is given by (6) of Appendix I and is equivalent to a set of four equations in the four large components of ψ which, following Breit, we denote by ψ_{33}, ψ_{34}, ψ_{43} and ψ_{44} respectively. Since the equation (6) of Appendix I is sufficient for all physical purposes and gives quantitative results correct to the order of $(v/c)^2$, we shall in the following sections be discussing the consequences following from this only.

The matrices σ^{I} and σ^{II} in (6) of Appendix I are the Pauli matrices and they operate on the suffixes 3 and 4. The operation rule for the product of any two matrices on ψ is still governed by (3), but now the summation for k or l extends over the numbers 3 and 4 only. One can verify that the equation $\mathrm{J}_x\psi = \mathrm{M}\hbar\psi$ is identical with the four equations given by (9), and the form of the four large components is therefore still given by the equations (10).

By solving the simultaneous differential equations (7), Appendix I, one can determine the functions ψ_{33}, ψ_{34}, ψ_{43} and ψ_{44} respectively. Thus a state ψ which we denote by the column vector $[\psi_{33}, \psi_{34}, \psi_{43}, \psi_{44}]$ consists in general of four non-zero components.

V. THE RUSSEL-SAUNDERS COUPLING

When the spin-orbit interaction is small compared to the electrostatic interaction of the two electrons, the terms involving $\mathbf{B}^{\mathrm{I}}$, $\mathbf{B}^{\mathrm{II}}$, C_{xy} as well as the last four terms in the expression for A in equation (6, Appendix I) could be ignored in the first approximation. This is the assumption underlying the case of the well-known Russel-Saunders coupling. The equations (7, Appendix I) now reduce to

$$\begin{aligned} &(\mathrm{H} - \mathrm{W})\,\psi_{33} = 0; && (\mathrm{H} - \mathrm{W})\,\psi_{34} = 0 \\ &(\mathrm{H} - \mathrm{W})\,\psi_{43} = 0; && (\mathrm{H} - \mathrm{W})\,\psi_{44} = 0 \end{aligned} \tag{11}$$

where H is the non-relativistic Hamiltonian of the system. The above equations are satisfied by four different states of the system in each of which all components, excepting one, are zero. Thus, solutions of (11) exist which have the form

$$\begin{aligned} &\psi_1 = [\psi_{33}, 0\ 0, 0]; && \psi_2' = [0, \psi_{34}, 0, 0] \\ &\psi_3' = [0, 0, \psi_{43}, 0]; && \psi_4 = [0, 0, 0, \psi_{44}] \end{aligned}$$

Since the spin-orbit coupling terms are neglected in the Hamiltonian (6, Appendix I), one can see that both

$$\mathrm{M}_x = m_x^{\mathrm{I}} + m_x^{\mathrm{II}} \qquad \text{and} \qquad \mathrm{S}_x = \frac{\hbar}{2}(\sigma_x^{\mathrm{I}} + \sigma_x^{\mathrm{II}})$$

are constants of motion in this case, and further ψ_1 and ψ_4 are states belonging to the eigenvalues $\hbar$ and $-\hbar$ of S_x respectively, whereas the states ψ_2' and ψ_3' have zero as the eigenvalue of S_x. From the form of ψ_{34} and ψ_{43} in (10), one can see that the states

$$\psi_2 = \psi_2' + \psi_3' = [0, \psi_{34}, \psi_{43}, 0]$$

and

$$\psi_3 = \psi_2' - \psi_3' = [0, \psi_{34}, -\psi_{43}, 0]$$

have the eigenvalue M for the x-component of the total orbital angular momentum and zero for the x-component of the total spin angular momentum. Further if

$$\Sigma^2 = \tfrac{1}{4}[(\sigma_x^{\mathrm{I}} + \sigma_x^{\mathrm{II}})^2 + (\sigma_y^{\mathrm{I}} + \sigma_y^{\mathrm{II}})^2 + (\sigma_z^{\mathrm{I}} + \sigma_z^{\mathrm{II}})^2]$$

one can verify from (3) that the states ψ_1, ψ_2 and ψ_4 are eigenstates of Σ^2 belonging to the eigenvalue 2 (or the value 1 for Σ), and the state ψ_3 has the eigenvalue zero for Σ. The former set of states are thus the well-known triplet states of two electron systems whereas the state ψ_3 represents the singlet state.

Now according to the Pauli Exclusion Principle, every state should be anti-symmetric with respect to an exchange of the two electrons. An exchange operator, which we denote by P, interchanges the spin states of the two electrons as well as their positions and thus under its influence, a component of the state $\psi_{mn}(1, 2)$ gets transformed into $\psi_{nm}(2, 1)$. The state

$$\psi = [\psi_{33}(1, 2), \psi_{34}(1, 2), \psi_{43}(1, 2), \psi_{44}(1, 2)]$$

therefore changes into $\psi = [\psi_{33}(2, 1), \psi_{43}(2, 1), \psi_{34}(2, 1), \psi_{44}(2, 1)]$ under the influence of P. In order to satisfy the Exclusion Principle, the following relations should therefore be obeyed by the components of a state: (1) $\psi_{33}(2, 1) = -\psi_{33}(1, 2)$; (2) $\psi_{34}(2, 1) = -\psi_{43}(1, 2)$ and (3) $\psi_{44}(2, 1) = -\psi_{44}(1, 2)$. One can see that the states ψ_1 and ψ_4 will be anti-symmetric if the components ψ_{33} and ψ_{44} are anti-symmetric functions of the position of the two electrons. Since ψ_{34} and ψ_{43} are solutions of the same Schroedinger equation in the Russel-Saunders approximation, the state ψ_2 will be anti-symmetric if its components ψ_{34} and ψ_{43} are such that $\psi_{34}(1, 2) = \psi_{43}(1, 2) = -\psi_{34}(2, 1) = -\psi_{43}(2, 1)$, and similarly the state ψ_3 will be anti-symmetric if

$$\psi_{34}(1, 2) = \psi_{34}(2, 1) = -\psi_{43}(1, 2) = -\psi_{43}(2, 1)$$

(*a*) *The symmetric and anti-symmetric states.*—Let $\psi_{nlm}(r_{a_1})$ ..... denote a complete set of eigenfunctions of a hydrogen atom whose nucleus is at position A. Then these functions form a complete basis for the expansion of any arbitrary single-valued function of the position $\mathbf{r}_1 = (x_1, y_1, z_1)$ of the electron 1. Similarly, the set of eigenfunctions $(\psi_{n'l'm'}(\mathbf{r}_{b_2})$ of a hydrogen atom with its nucleus in position B form a complete set of eigenfunctions for the expansion of an arbitrary function of the position $\mathbf{r}_2$ of the electron 2. Then, by a well-known theorem,[4] the set of functions

$$\psi_{nlm}(r_{a_1})\,\psi_{n'l'm'}(r_{b_2}) \begin{pmatrix} n = 1, 2 \ldots\ldots\ldots \\ n' = 1, 2 \ldots\ldots\ldots \end{pmatrix}$$

form a complete basis for the expansion of an arbitrary function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ of the two electrons, that vanishes when $r_1 \to \infty$ and $r_2 \to \infty$. Thus we can write

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nn'} \mathrm{F}_{nn'}\,\psi_n(\mathbf{r}_{a_1})\,\psi_{n'}(\mathbf{r}_{b_2}) \qquad (12)$$

where we have written n and n' for the set of three quantum numbers (n, l, m) and (n', l', m') of the hydrogen atoms.

Now if the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric with respect to an interchange of the two electrons, we get from (12) by interchanging the suffixes (1) and (2) that

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nn'} \mathrm{F}_{nn'} \psi_n(\mathbf{r}_{a_2}) \psi_{n'}(\mathbf{r}_{b_1}) \tag{13}$$

The above equation alternatively follows from the expansion of $\psi(\mathbf{r}_1, \mathbf{r}_2)$ in terms of the set of functions $\psi_n(\mathbf{r}_{a_2}) \psi_{n'}(\mathbf{r}_{b_1}) \ldots$. which also form a complete basis for the expansion of a function of the two electrons.

By adding (12) and (13)* we see that any symmetric function of the electrons 1 and 2 can be written as

$$\psi^+(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nn'} f_{nn'} [\psi_n(\mathbf{r}_{a_1}) \psi_{n'}(\mathbf{r}_{b_2}) + \psi_n(\mathbf{r}_{a_2}) \psi_{n'}(\mathbf{r}_{b_1}) \tag{14}$$

where $f_{nn'} = \frac{1}{2} \mathrm{F}_{nn'}$. The suffix $+$ has been used to indicate that the function ψ is symmetric with respect to an interchange of the electrons.

In the same way we can see that an anti-symmetric function $\psi^-(\mathbf{r}_1, \mathbf{r}_2)$ of the electrons has the form

$$\psi^-(r_1, r_2) = \sum_{nn'} g_{nn'} [\psi_n(\mathbf{r}_{a_1}) \psi_{n'}(\mathbf{r}_{b_2}) - \psi_n(\mathbf{r}_{a_2}) \psi_{n'}(\mathbf{r}_{b_1})] \tag{15}$$

(*b*) *The singlet state.*—We have seen before that the singlet state ψ_3 is represented by the vector $[0, \psi_{34}^+, -\psi_{34}^+, 0]$ where ψ_{34}^+ is a symmetric function of the two electrons. Now from the equations (10) it follows that ψ_{34} has the form given by

$$\psi_{34} = f_{34}(r_1, r_2, \theta_1, \theta_2)\, e^{i(m_1\phi_1 + m_2\phi_2)} \tag{10 a}$$

where m_1 and m_2 are integers satisfying the relation $m_1 + m_2 = \mathrm{M}$. Thus the general form of ψ_{34} consists of a superposition of terms of the type (10 *a*) for all integral values of m_1 and m_2 satisfying the condition $m_1 + m_2 = \mathrm{M}$.

Let us consider the case where the component of the total angular momentum parallel to the axis of the molecule is zero, *i.e.*, $m_1 + m_2 = 0$ or $m_1 = -m_2$. It is well known that the ground state of the hydrogen molecule belongs to this species. Thus from (14) and (10 *a*) it follows that the eigenfunction of the ground state is given by

$$\psi_{34}^+(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nlm} \sum_{n'l'} f_{nn'} [\psi_{nlm}(\mathbf{r}_{a_1}) \psi_{n'l'-m}(\mathbf{r}_{b_2}) + \psi_{nlm}(\mathbf{r}_{a_2}) \psi_{n'l'-m}(\mathbf{r}_{b_1})] \tag{16}$$

* We assume the absolute convergence of these series.

The first term of the above series is

$$[\psi_{100}(\mathbf{r}_{a_1})\,\psi_{100}(\mathbf{r}_{b_2}) + \psi_{100}(\mathbf{r}_{a_2})\,\psi_{100}(\mathbf{r}_{b_1})] \tag{17}$$

which is the well-known Heitler-London wave function. This function explains qualitatively in a satisfactory manner the chemical binding of the hydrogen molecule, but quantitatively it gives a value of 3·14 e.v. for the binding energy of the molecule, the observed value being 4·72 e.v. The quantitative inaccuracy of the Heitler-London function is not surprising when we recall that it is only the first term in the expansion of the wave function in terms of symmetric wave functions built from the hydrogen atomic orbitals. Since the discrepancy between the energy value derived from (17) and the experimentally observed one is not very large, one can hope that the series (16) converges rather rapidly and that the addition of a few more terms to (17) will lead one to the correct value for the binding energy of the molecule.

(*c*) *The triplet states.*—As an example of the triplet states, consider the state ψ_1 which is described by a non-vanishing anti-symmetric component $\psi_{33}^{-}(\mathbf{r}_1, \mathbf{r}_2)$ and three vanishing components. From (10) we have

$$\psi_{33} = f_{33}(r_1, r_2, \theta_1, \theta_2)\, e^{i(m_1\phi_1 + m_2\phi_2)} \tag{18}$$

where $m_1 + m_2 = (\mathrm{M} - 1)$.

Since the component of the total spin angular momentum for this state is $\hbar$, the component of the total orbital angular momentum is equal to $(\mathrm{M} - 1)\,\hbar$. The general form of ψ_{33} will consist of a superposition of terms of the type (18) for all integral values of m_1 and m_2 satisfying the relation $m_1 + m_2 = (\mathrm{M} - 1)$. Thus from (15) it follows that ψ_{33}^{-} is given by

$$\psi_{33}^{-}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nlm} \sum_{n'l'm'} g_{nn'} [\psi_{nlm}(\mathbf{r}_{a_1})\,\psi_{n'l'm'}(\mathbf{r}_{b_2}) - \psi_{nlm}(\mathbf{r}_{a_2})\,\psi_{n'l'm'}(\mathbf{r}_{b_1})] \tag{19}$$

where $m + m' = (\mathrm{M} - 1)$.

In other words, the state ψ_1 is a superposition of all anti-symmetric molecular states for which the component of the total orbital angular momentum is equal to $(\mathrm{M} - 1)\,\hbar$. In the same way we can obtain the wave function for the state ψ_4 by superposing anti-symmetric molecular states have the eigenvalue $(\mathrm{M} + 1)\,\hbar$ for the component of the total orbital angular momentum parallel to the axis of the molecule.

Regarding the state ψ_2 we shall consider the particular case $\mathrm{M} = 0$. ψ_2 is described by the vector $[0, \psi_{34}^{-}, \psi_{34}^{-}, 0]$ where ψ_{34}^{-} is anti-symmetric

with respect to an interchange of the two electrons. From (15) and (10 *a*) it follows that the form of ψ_{34}^{-} is given by

$$\psi_{34}^{-}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{nlm} \sum_{n'l'} g_{nn'} [\psi_{nlm}(\mathbf{r}_{a_1}) \psi_{n'l'-m}(\mathbf{r}_{b_2}) - \psi_{nlm}(\mathbf{r}_{a_2}) \psi_{n'l'-m}(\mathbf{r}_{b_1}) \quad (20)$$

The first term of the above series is

$$[\psi_{100}(\mathbf{r}_{a_1}) \psi_{100}({}_b\mathbf{r}_2) - \psi_{100}({}_a\mathbf{r}_2) \psi_{100}(\mathbf{r}_{b_1})] \quad (21)$$

It is a well-known fact that this function leads to an unstable chemical state.

(*d*) *The case of C_2 and O_2.*—From (19) or (20), it follows that the wave function for a triplet state is a superposition of a number of terms each of which is anti-symmetric with respect to an interchange of the two electrons. Further, all the terms in a series belong to the same species, *i.e.*, the states belonging to these terms have all the same eigenvalue for the x-component of the total orbital angular momentum.

According to the Heitler-London theory, the ground state of the hydrogen molecule is the singlet state and the triplet states are unstable. The theory therefore requires as an essential condition for a stable bond that the spins of the two electrons should be antiparallel. This rule is obeyed by a large class of molecules, but nevertheless, exceptions are also present of which we may cite the examples of C_2 and O_2. The ground state of C_2 is the state designated in spectroscopic notation by ${}^3\Pi_u$ whereas for oxygen, the ground state is ${}^3\Sigma_g^{-}$. Oxygen is in addition paramagnetic. Heitler[6] and Nordheim-Poschl[7] showed that by adding to the wave function (21) a few more terms of the same species, or in other words, by taking into account the interaction between states of the same species, the deviations between theory and experiment can be removed. Now in the Russel-Saunders approximation, Σ has the value 1 for the triplet states and Σ_z has the values 1, 0, -1 respectively for the states ψ_1, ψ_2 and ψ_4. Further each term in (19) or (20) corresponds to the same value of the component of the total orbital angular momentum parallel to the axis of the molecule. The expansion (19) is, therefore, nothing but a superposition of states of the same species. Relativistic theory offers thus a clear explanation of the facts relating to C_2 and O_2 and brings about naturally the concept of interaction of states of the same species.

VI. STRONG SPIN-ORBIT COUPLING

The discussion of the last section holds good only for the case of Russel-Saunders coupling. Strictly speaking, the Russel-Saunders coupling and the

j-j coupling are two extreme ideal cases and the coupling in most cases is intermediate. When the spin-orbit interaction is strong compared to the electrostatic interaction of the two electrons, the above discussion will break down. In such a case, only the component of the total angular momentum along the axis is a constant of motion and none of the quantities Σ, Σ_x and M_x is a constant of motion. An eigenstate of the energy will be an eigenstate of J_x also and conversely every state of the system will specify, besides the energy, only the x-component of the total angular momentum. For the case of strong spin-orbit coupling, the usual spectroscopic notation which presumes that all the quantities Σ, Σ_x and M_x are constants of motion, is therefore inconsistent with theoretical considerations and requires modification.

When the spin-orbit coupling is strong, the solution of the equations (7, Appendix I) will lead to non-zero values for all the four components of the wave function. Further it follows from equations (6) and (7) of Appendix I that a state will be anti-symmetric with respect to an interchange of electrons only if the components have the following properties:

(1) $\psi_{33}(2, 1) = -\psi_{33}(1, 2)$;

(2) $\psi_{34}(2, 1) = -\psi_{43}(1, 2)$;

(3) $\psi_{44}(2, 1) = -\psi_{44}(1, 2)$.

Thus ψ_{33} and ψ_{44} are anti-symmetric functions, while ψ_{34} or ψ_{43} can be a mixture of both symmetric and anti-symmetric functions. The form of the former components is therefore given by (15) while the latter can be expanded as a series of the type (12). Now the energy of the system is given by

$$W = \frac{\int \psi^* H \psi d\tau_1 d\tau_2}{\int \psi^* \psi d\tau_1 d\tau_2} \tag{22}$$

where ψ^* is the transpose of the vector ψ and is given by the *row* vector $[\psi_{33}^*, \psi_{34}^*, \psi_{43}^*, \psi_{44}^*]$.

In practice, the computation of the energy will be facilitated if (1) the series for the function ψ_{33}, etc., are terminated at a particular point and their coefficients determined by the variational principle and (2) if use is made of the tables giving the values of exchange, coulomb and other related integrals.[8, 9, 10]

We can now interpret the quantities ψ_{33}^2, $\psi_{34}^2 + \psi_{43}^2$ and ψ_{44}^2 as the probabilities of finding the spins of the electrons respectively (1) parallel to the x-axis, (2) opposite to each other and (3) parallel to the negative direction of the x-axis. The ground state of the molecule will be the state having the

least value for the energy of all the states, subject to the condition that it is stable besides.

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Appendix I

For the sake of easy reference, we collect here some of the results and equations of Breit that are made use of in the paper. The relativistic wave equation of Breit is given by

$$\left[p_0 + \sum_{k=1,2,3} (\alpha_k^{\mathrm{I}} p_k^{\mathrm{I}} + \alpha_k^{\mathrm{II}} p_k^{\mathrm{II}}) + (\alpha_4^{\mathrm{I}} + \alpha_4^{\mathrm{II}})\, mc + \frac{e^2}{2cr} \left\{ \sum_k \alpha_k^{\mathrm{I}} \alpha_k^{\mathrm{II}} + \frac{(\boldsymbol{\alpha}^{\mathrm{I}} \cdot \mathbf{r})(\boldsymbol{\alpha}^{\mathrm{II}} \cdot \mathbf{r})}{r^2} \right\} \right] \psi = 0 \qquad (1)$$

Here p_0, p^{I} and p^{II} are given by equations (2) of Section II. The wave function ψ has sixteen components which are denoted by ψ_{mn} ($m, n = 1, 2, 3, 4$). The matrices α^{I} and α^{II} are the usual Dirac matrices, but now they operate on the suffixes I and II respectively. They are given by

$$\alpha_1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}; \quad \alpha_2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}; \qquad (2)$$

$$\alpha_3 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}; \quad \alpha_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

If we set

$$\alpha_1 = \rho_1 \sigma_1; \quad \alpha_2 = \rho_1 \sigma_2; \quad \alpha_3 = \rho_1 \sigma_3, \qquad (3)$$

where

$$\sigma_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}; \quad \sigma_2 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix};$$

$$\sigma_3 = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}; \quad \rho_1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

equation (1) becomes

$$\left\{ \begin{aligned} & p_0 + \rho_1^{\mathrm{I}} (\sigma^{\mathrm{I}} \cdot \mathbf{p}^{\mathrm{I}}) + \rho_1^{\mathrm{II}} (\sigma^{\mathrm{II}} \cdot \mathbf{p}^{\mathrm{II}}) + (\alpha_4^{\mathrm{I}} + \alpha_4^{\mathrm{II}})\, mc \\ & \quad + \frac{e^2}{2cr} \left[(\rho_1^{\mathrm{I}} \sigma^{\mathrm{I}} \cdot \rho_1^{\mathrm{II}} \sigma^{\mathrm{II}}) + \frac{(\rho_1^{\mathrm{I}} \alpha^{\mathrm{I}} \cdot \mathbf{r})\, (\rho_1^{\mathrm{II}} \alpha^{\mathrm{II}} \cdot r)}{r^2} \right] \end{aligned} \right\} \psi = 0 \qquad (5)$$

It follows that the Hamiltonian of the system is given by equation (5) of Section II.

Next the Breit equation in the Schroedinger-Pauli form is given by

$$\begin{aligned} \Big\{ & \mathrm{E} - 2mc^2 + e\mathrm{V} - \frac{1}{2m} [(p^{\mathrm{I}})^2 + (p^{\mathrm{II}})^2] + \frac{(p^{\mathrm{I}})^4 + (p^{\mathrm{II}})^4}{8m^3c^3} \\ & + \frac{e^2}{2m^2c^2} [r^{-1} (\mathbf{p}^{\mathrm{I}}, \mathbf{p}^{\mathrm{II}}) + r^{-3} (x_i^{\mathrm{II}} - x_i^{\mathrm{I}}) (x_j^{\mathrm{II}} - x_j^{\mathrm{I}})\, p_i^{\mathrm{I}} p_j^{\mathrm{II}}] \\ & + \frac{eh}{4\pi mc} [(\mathbf{H}^{\mathrm{I}}, \sigma^{\mathrm{I}}) + (\mathbf{H}^{\mathrm{II}}, \sigma^{\mathrm{II}})] + \frac{ehi}{8\pi m^2c^2} [(\mathscr{E}^{\mathrm{I}}, \mathbf{p}^{\mathrm{I}}) + (\mathscr{E}^{\mathrm{II}}, \mathbf{p}^{\mathrm{II}})] \\ & + \frac{eh}{8\pi mc^2} \left[\left(\mathscr{E}^{\mathrm{I}} \times \frac{\mathbf{p}^{\mathrm{I}}}{m}, \sigma^{\mathrm{I}} \right) + \left(\mathscr{E}^{\mathrm{II}} \times \frac{\mathbf{p}^{\mathrm{II}}}{m}, \sigma^{\mathrm{II}} \right) \right. \\ & \left. + 2e \left(\frac{\mathbf{r}^{\mathrm{I}} - \mathbf{r}^{\mathrm{II}}}{r^3} \times \frac{\mathbf{p}^{\mathrm{II}}}{m}, \sigma^{\mathrm{I}} \right) + 2e \left(\frac{\mathbf{r}^{\mathrm{II}} - \mathbf{r}^{\mathrm{I}}}{r^3} \times \frac{\mathbf{p}^{\mathrm{I}}}{m}, \sigma^{\mathrm{II}} \right) \right] \\ & - \left(\frac{eh}{4\pi mc} \right)^2 \langle (\nabla^{\mathrm{II}} \sigma^{\mathrm{I}})\, (\nabla^{\mathrm{I}} \sigma^{\mathrm{II}})\, r^{-1} \rangle \Big\} \psi = 0 \end{aligned} \qquad (6)$$

where

$$\mathbf{H}^{\mathrm{I}} = \mathrm{curl}\, \mathbf{A}^{\mathrm{I}}, \quad \mathbf{H}^{\mathrm{II}} = \mathrm{curl}\, \mathbf{A}^{\mathrm{II}}$$

$$\mathscr{E}^{\mathrm{I}} = -\,\mathrm{grad}^{\mathrm{I}}\, \mathrm{V} = -\left(\frac{\partial}{\partial x^{\mathrm{I}}}, \frac{\partial}{\partial y^{\mathrm{I}}}, \frac{\partial}{\partial z^{\mathrm{I}}} \right) \mathrm{V};$$

$$\mathrm{V} = \phi^{\mathrm{I}} + \phi^{\mathrm{II}} - \frac{e}{r}.$$

$\langle\,\rangle$ means the differential operators $\mathbf{p}^{\mathrm{I}}$, $\mathbf{p}^{\mathrm{II}}$ apply only within the $\langle\,\rangle$. The σ's are the Pauli matrices and have the representations given by

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Let us write

$$\mathrm{E} - 2mc^2 = \mathrm{W};$$

$$\mathrm{A} = e\mathrm{V} - \frac{1}{2m}\{(p^{\mathrm{I}})^2 + (p^{\mathrm{II}})^2\} + \frac{(p^{\mathrm{I}})^4 + (p^{\mathrm{II}})^4}{8m^3c^3}$$

$$+ \frac{e^2}{2m^2c^2}[r^{-1}\,\mathbf{p}^{\mathrm{I}} \cdot \mathbf{p}^{\mathrm{II}} + \Sigma\, r^{-3}(x_i^{\mathrm{II}} - x_i^{\mathrm{I}})(x_j^{\mathrm{II}} - x_j^{\mathrm{I}})\, p_i^{\mathrm{I}} p_j^{\mathrm{II}}]$$

$$+ \frac{ehi}{8\pi m^2c^2}\{(\mathscr{E}^{\mathrm{I}}, \mathbf{p}^{\mathrm{I}}) + (\mathscr{E}^{\mathrm{II}}, \mathbf{p}^{\mathrm{II}})\}.$$

$$\mathrm{B}^{\mathrm{I}} = \frac{eh}{8\pi mc^2}\left[\mathscr{E}^{\mathrm{I}} \times \frac{\mathbf{p}^{\mathrm{I}}}{m} + 2e\,\frac{\mathbf{r}^{\mathrm{I}} - \mathbf{r}^{\mathrm{II}}}{r^3} \times \frac{p^{\mathrm{II}}}{m}\right] = (\mathrm{B}_x{}^{\mathrm{I}}, \mathrm{B}_y{}^{\mathrm{I}}, \mathrm{B}_z{}^{\mathrm{I}})$$

$$\mathrm{B}^{\mathrm{II}} = \frac{eh}{8\pi mc^2}\left[\mathscr{E}^{\mathrm{II}} \times \frac{p^{\mathrm{II}}}{m} + 2e\,\frac{\mathbf{r}^{\mathrm{II}} - \mathbf{r}^{\mathrm{I}}}{r^3} \times \frac{\mathbf{p}^{\mathrm{I}}}{m}\right] = (\mathrm{B}_x{}^{\mathrm{II}}, \mathrm{B}_y{}^{\mathrm{II}}, \mathrm{B}_z{}^{\mathrm{II}})$$

and

$$-\left(\frac{eh}{4\pi mc}\right)^2 \langle(\nabla^{\mathrm{II}}, \sigma^{\mathrm{I}})(\nabla^{\mathrm{I}}, \sigma^{\mathrm{II}})\, r^{-1}\rangle = \Sigma\, \mathrm{C}_{xy}\sigma_x{}^{\mathrm{I}}\sigma_y{}^{\mathrm{II}}$$

where

$$\mathrm{C}_{xy} = -\left(\frac{eh}{4\pi mc}\right)^2 \frac{\partial}{\partial x^{\mathrm{II}}}\frac{\partial}{\partial y^{\mathrm{I}}}\, r^{-1}.$$

Then the equation (6) is equivalent to the following four equations:

$$\begin{aligned}(\mathrm{A} + \mathrm{B}_x{}^{\mathrm{I}} + \mathrm{B}_x{}^{\mathrm{II}} + \mathrm{C}_{xx} + \mathrm{W})\,\psi_{33} + (\mathrm{B}_y{}^{\mathrm{II}} - i\mathrm{B}_z{}^{\mathrm{II}} + \mathrm{C}_{xy} - i\mathrm{C}_{xz})\,\psi_{34} \\ + (\mathrm{B}_y{}^{\mathrm{I}} - i\mathrm{B}_z{}^{\mathrm{I}} + \mathrm{C}_{yx} - i\mathrm{C}_{zx})\,\psi_{43} + (\mathrm{C}_{yy} - \mathrm{C}_{zz} \\ - i\mathrm{C}_{yz} + \mathrm{C}_{zy})\,\psi_{44} = 0.\end{aligned}$$

$$\begin{aligned}(\mathrm{B}_y{}^{\mathrm{II}} + i\mathrm{B}_z{}^{\mathrm{II}} + \mathrm{C}_{xy} + i\mathrm{C}_{xz})\,\psi_{33} + (\mathrm{A} + \mathrm{B}_x{}^{\mathrm{I}} - \mathrm{B}_x{}^{\mathrm{II}} - \mathrm{C}_{xx} + \mathrm{W})\,\psi_{34} \\ + (\mathrm{C}_{yy} + \mathrm{C}_{zz})\,\psi_{43} + (\mathrm{B}_y{}^{\mathrm{I}} - i\mathrm{B}_z{}^{\mathrm{I}} - \mathrm{C}_{yx} + i\mathrm{C}_{zx})\,\psi_{44} = 0\end{aligned} \tag{7}$$

$$\begin{aligned}(\mathrm{B}_y{}^{\mathrm{I}} + i\mathrm{B}_z{}^{\mathrm{I}} + \mathrm{C}_{yx} + i\mathrm{C}_{zx})\,\psi_{33} + (\mathrm{C}_{yy} + \mathrm{C}_{zz})\,\psi_{34} \\ + (\mathrm{A} + \mathrm{B}_x{}^{\mathrm{II}} - \mathrm{B}_x{}^{\mathrm{I}} - \mathrm{C}_{xx} + \mathrm{W})\,\psi_{43} + (\mathrm{B}_y{}^{\mathrm{II}} - i\mathrm{B}_z{}^{\mathrm{II}} - \mathrm{C}_{xy} \\ + i\mathrm{C}_{xz})\,\psi_{44} = 0\end{aligned}$$

$$(C_{yy} - C_{zz} + i\overline{C_{yz} + C_{zy}})\,\psi_{33} + (B_y^{I} + iB_z^{I} - C_{yx} - iC_{zx})\,\psi_{34} + (B_y^{II} + iB_z^{II} - C_{xy} - iC_{xz})\,\psi_{43} + (A - B_x^{I} - B_x^{II} + C_{xx} + W)\,\psi_{44} = 0.$$

APPENDIX II

Proof of the relation $J_xH - HJ_x = 0$.—We have seen that the Hamiltonian for a hydrogen molecule is given by

$$H = -e(\phi^{I} + \phi^{II}) + \frac{e^2}{r} - \rho_1^{I} c\,(\sigma^{I} \cdot \mathbf{p}^{I}) - \rho_1^{II} c\,(\sigma^{II} \cdot \mathbf{p}^{II}) - m_0c^2\,(\alpha_4^{I} + \alpha_4^{II}) - \frac{e^2}{2r}\left\{\rho^{I}\sigma^{I} \cdot \rho_1^{II}\sigma^{II}) + \frac{(\rho_1\sigma^{I} \cdot \mathbf{r})\ (\rho_1^{II}\sigma^{II} \cdot \mathbf{r})}{r^2}\right\} \tag{1}$$

where

$$\phi^{I} = e\left(\frac{1}{r_{a_1}} + \frac{1}{r_{b_1}}\right) \qquad \text{and} \qquad \phi^{II} = e\left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_2}}\right);$$

r is the interelectronic distance. Each of the angular momentum variables m_x^{I} and m_x^{II} commutes with r_{a_1}, r_{b_1}, r_{a_2} and r_{b_2} and hence with the potentials ϕ^{I} and ϕ^{II}. Further

$$[m_x^{I} + m_x^{II},\ r^2] = [m_x^{I} + m_x^{II},\ \Sigma x_1^2 + \Sigma x_2^2 - 2\Sigma x_1x_2] = -2(y_1z_2 - y_2z_1) - 2(y_2z_1 - y_1z_2) = 0 \tag{2}$$

$(m_x^{I} + m_x^{II})$ commutes with r^2 and hence with any function of r^2, particularly with $1/r$ and $1/r^3$.

Now

$$i\hbar\,(\dot{m}_x^{I} + \dot{m}_x^{II}) = (m_x^{I} + m_x^{II})\,H - H\,(m_x^{I} + m_x^{II}) \tag{3}$$

Since $(m_x^{I} + m_x^{II})$ commutes with ϕ^{I}, ϕ^{II}, $1/r$ and $1/r^3$, we have

$$i\hbar\,(\dot{m}_x^{I} + \dot{m}_x^{II}) = -c\rho_1^{I}\{m_x^{I}(\sigma^{I} \cdot \mathbf{p}^{I}) - (\sigma^{I} \cdot p^{I})\,m_x^{I}\} - c\rho_1^{II}\{m_x^{II}(\sigma^{II} \cdot p^{II}) - (\sigma^{II} \cdot p^{II})\,m_x^{II}\} - \frac{e^2}{2r^3}\left\{\begin{matrix}(m_x^{I} + m_x^{II})\,(\rho_1^{I}\sigma^{I} \cdot \mathbf{r})\,(\rho_1^{II}\sigma^{II} \cdot \mathbf{r}) \\ -(\rho_1^{I}\sigma^{I} \cdot \mathbf{r})\,(\rho_1^{II}\sigma^{II} \cdot \mathbf{r})\,(m_x^{I} + m_x^{II})\end{matrix}\right\} \tag{4}$$

Now

$$\{m_x^{I}(\sigma^{I} \cdot \mathbf{p}^{I}) - (\sigma^{I} \cdot \mathbf{p}^{I})\,m_x^{I}\} = (\sigma^{I},\ m_x^{I}\mathbf{p}^{I} - \mathbf{p}^{I}m_x^{I}) = i\hbar\,(\sigma_2p_3 - \sigma_3p_2)^{I} \tag{5}$$

Similarly

$$\{m_x{}^{\mathrm{II}}(\sigma^{\mathrm{II}} \cdot p^{\mathrm{II}}) - (\sigma^{\mathrm{II}} \cdot p^{\mathrm{II}})\, m_x{}^{\mathrm{II}}\} = i\hbar\,(\sigma_2 p_3 - \sigma_3 p_2)^{\mathrm{II}} \tag{6}$$

Next the following Poisson bracket relations can be verified:

$$\left[m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}},\ \frac{(x_2 - x_1)\,(y_2 - y_1)}{r^3}\right] = \frac{(x_2 - x_1)\,(z_2 - z_1)}{r^3}\ ;$$

$$\left[m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}},\ \frac{(x_2 - x_1)\,(z_2 - z_1)}{r^3}\right] = \frac{(x_2 - x_1)\,(y_2 - y_1)}{r^3}\ ;$$

$$\left[m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}},\ \frac{(y_2 - y_1)\,(z_2 - z_1)}{r^3}\right] = \left[\frac{(z_2 - z_1)^2 - (y_2 - y_1)^2}{r^3}\right];$$

$$\left[m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}},\ \frac{(y_2 - y_1)^2}{r^3}\right] = \frac{2\,(y_2 - y_1)\,(z_2 - z_1)}{r^3}\ ;$$

$$\left[m_x{}^{\mathrm{I}} + m_x{}^{\mathrm{II}},\ \frac{(z_2 - z_1)^2}{r^3}\right] = \frac{-\,2\,(y_2 - y_1)\,(z_2 - z_1)}{r^3}\,. \tag{7}$$

Hence if we denote the components of the vectors $\rho_1{}^{\mathrm{I}}\sigma^{\mathrm{I}}$ and $\rho_1{}^{\mathrm{II}}\sigma^{\mathrm{II}}$ by

$$(a_x{}^{\mathrm{I}},\ a_y{}^{\mathrm{I}},\ a_z{}^{\mathrm{I}}) \qquad \text{and} \qquad (a_x{}^{\mathrm{II}},\ a_y{}^{\mathrm{II}},\ a_z{}^{\mathrm{II}}),$$

we get from (3), (4), (5), (6) and (7) that

$$\begin{aligned} & i\hbar\,(\dot{m}_x{}^{\mathrm{I}} + \dot{m}_x{}^{\mathrm{II}}) \\ & \quad = -\,i\hbar\,c\rho_1{}^{\mathrm{I}}\,(\sigma_2 p_3 - \sigma_3 p_2)^{\mathrm{I}} - i\hbar\,c\rho_1{}^{\mathrm{II}}\,(\sigma_2 p_3 - \sigma_3 p_2)^{\mathrm{II}} \\ & \quad\quad - \frac{i\hbar e^2}{2r^3}\left\{\begin{array}{l} (a_x{}^{\mathrm{I}} a_y{}^{\mathrm{II}} + a_y{}^{\mathrm{I}} a_x{}^{\mathrm{II}})\,(x_2 - x_1)\,(z_2 - z_1) \\ \quad - (a_x{}^{\mathrm{I}} a_z{}^{\mathrm{II}} + a_z{}^{\mathrm{I}} a_x{}^{\mathrm{II}})\,(x_2 - x_1)\,(y_2 - y_1) \\ \quad + (a_y{}^{\mathrm{I}} a_z{}^{\mathrm{II}} + a_z{}^{\mathrm{I}} a_y{}^{\mathrm{II}})\,[(z_2 - z_1)^2 - (y_2 - y_1)^2] \\ \quad + 2\,(a_y{}^{\mathrm{I}} a_y{}^{\mathrm{II}} - a_z{}^{\mathrm{I}} a_z{}^{\mathrm{II}})\,(y_2 - y_1)\,(z_2 - z_1) \end{array}\right\} \end{aligned} \tag{8}$$

Next we have

$$\begin{aligned} (\sigma_x{}^{\mathrm{I}}\sigma^{\mathrm{I}} - \sigma^{\mathrm{I}}\sigma_x{}^{\mathrm{I}},\ \mathbf{p}^{\mathrm{I}}) &= 2i\,(\sigma_3 p_2 - \sigma_2 p_3)^{\mathrm{I}} \\ (\sigma_x{}^{\mathrm{II}}\sigma^{\mathrm{II}} - \sigma^{\mathrm{II}}\sigma_x{}^{\mathrm{II}},\ \mathbf{p}^{\mathrm{II}}) &= 2i\,(\sigma_3 p_2 - \sigma_2 p_3)^{\mathrm{II}} \end{aligned} \tag{9}$$

Also

$$\left[\sigma_x{}^{\mathrm{I}} + \sigma_x{}^{\mathrm{II}},\ \frac{(\rho_1{}^{\mathrm{I}} r_1{}^{\mathrm{I}} \cdot \rho_1{}^{\mathrm{II}} \sigma^{\mathrm{II}})}{r^3}\right] = 0 \tag{10}$$

Further

$$\sigma_x^{\mathrm{I}}(\rho_1^{\mathrm{I}}\omega^{\mathrm{I}}\cdot\mathbf{r})(\rho_1^{\mathrm{II}}\omega^{\mathrm{II}}\cdot\mathbf{r})-(\rho_1^{\mathrm{I}}\omega^{\mathrm{I}}\cdot\mathbf{r})(\rho_1^{\mathrm{II}}\omega^{\mathrm{II}}\cdot\mathbf{r})\sigma_x^{\mathrm{I}}$$
$$=2i\{a_z^{\mathrm{I}}(y_2-y_1)-a_y^{\mathrm{I}}(z_2-z_1)\}\{a_x^{\mathrm{II}}(x_2-x_1)+a_y^{\mathrm{II}}(y_2-y_1)+a_z^{\mathrm{II}}(z_2-z_1)\}$$
$$\sigma_x^{\mathrm{II}}(\rho_1^{\mathrm{I}}\omega^{\mathrm{I}}\cdot\mathbf{r})(\rho_1^{\mathrm{II}}\omega^{\mathrm{II}}\cdot\mathbf{r})-(\rho_1^{\mathrm{I}}\omega^{\mathrm{I}}\cdot\mathbf{r})(\rho_1^{\mathrm{II}}\omega^{\mathrm{II}}\cdot\mathbf{r})\sigma_x^{\mathrm{II}}$$
$$=2i\{a_z^{\mathrm{II}}(y_2-y_1)-a_y^{\mathrm{II}}(z_2-z_1)\}\{a_x^{\mathrm{I}}(x_2-x_1)+a_y^{\mathrm{I}}(y_2-y_1)+a_z^{\mathrm{I}}(z_2-z_1)\} \tag{11}$$

From (9), (10) and (11), we get

$$i\hbar(\dot{\sigma}_x^{\mathrm{I}}+\dot{\sigma}_x^{\mathrm{II}})$$
$$=(\sigma_x^{\mathrm{I}}+\sigma_x^{\mathrm{II}})\mathrm{H}-\mathrm{H}(\sigma_x^{\mathrm{I}}+\sigma_x^{\mathrm{II}})$$
$$=-2ic\rho_1^{\mathrm{I}}(\sigma_3p_2-\sigma_2p_3)^{\mathrm{I}}-2ic\rho_1^{\mathrm{II}}(\sigma_3p_2-\sigma_2p_3)$$
$$-\frac{2ie^2}{2r^3}\left\{\begin{array}{l}(a_x^{\mathrm{I}}a_z^{\mathrm{II}}+a_z^{\mathrm{I}}a_x^{\mathrm{II}})(y_2-y_1)(x_2-x_1)\\ +(a_z^{\mathrm{I}}a_y^{\mathrm{II}}+a_z^{\mathrm{II}}a_y^{\mathrm{II}})\{(y_2-y_1)^2-(z_2-z_1)^2\}\\ +2(a_z^{\mathrm{I}}a_z^{\mathrm{II}}-a_y^{\mathrm{I}}a_y^{\mathrm{II}})(y_2-y_1)(z_2-z_1)\\ -(a_y^{\mathrm{I}}a_x^{\mathrm{II}}+a_y^{\mathrm{II}}a_x^{\mathrm{I}})(z_2-z_1)(x_2-x_1)\end{array}\right\} \tag{12}$$

From (8) and (12) it follows that

$$\dot{m}_x^{\mathrm{I}}+\dot{m}_x^{\mathrm{II}}+\frac{\hbar}{2}(\dot{\sigma}_x^{\mathrm{I}}+\dot{\sigma}_x^{\mathrm{II}})=0.$$

Or, in other words,

$$\mathrm{J}_x=m_x^{\mathrm{I}}+m_x^{\mathrm{II}}+\frac{\hbar}{2}(\sigma_x^{\mathrm{I}}+\sigma_x^{\mathrm{II}})\text{ is a constant of motion.}$$

Fields possessing cylindrical symmetry.—Though the above result has been proved for the case of a hydrogen molecule only, it holds good in general for any system of two electrons moving in a field possessing cylindrical symmetry. If the x-axis is chosen as the axis of symmetry, the potentials ϕ^{I} and ϕ^{II} in this case are functions of two variables only, *i.e.*, $\phi^{\mathrm{I}}=\phi^{\mathrm{I}}(x_1, r_1)$ and $\phi^{\mathrm{II}}=\phi^{\mathrm{II}}(x_2, r_2)$, r_1 and r_2 being the distances of the electrons from the origin. Since $\mathrm{M}_x=m_x^{\mathrm{I}}+m_x^{\mathrm{II}}$ commutes with all the variables x_1, x_2, r_1 and r_2, it commutes with the first term in the Hamiltonian (1). The remaining terms do not involve ϕ^{I} or ϕ^{II} and are the same as for the hydrogen molecule. Thus for a system of two electrons moving in a field of cylindrical symmetry, the component of the total angular momentum along the axis of symmetry is a constant of motion. Since for most diatomic molecules and individual bonds in complex molecules the charge cloud approximately satisfies cylindrical symmetry, the above result can be applied to such cases also.

THE CRYSTAL STRUCTURE OF L-TYROSINE HYDROHALIDES

Part II. L-Tyrosine Hydrochloride

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Introduction

The structure of L-tyrosine hydrobromide which is isomorphous with the hydrochloride has been discussed in the previous paper (Srinivasan, 1959, hereafter referred to as Part I). The structure had been solved by the application of the Difference-Patterson (Kartha and Ramachandran, 1955) and minimum function (Buerger, 1951) methods. The refinement of the structure of the hydrochloride was taken up for the sake of confirmation and elucidation of the various features found in the other compound. The details are given in this paper.

Experimental

The crystallographic and other experimental data are available in the previous paper (Part I) and are summarised here for convenience. L-tyrosine hydrochloride ($C_9H_{11}NO_3HCl$) belongs to the monoclinic system with space group $P2_1$. The unit cell dimensions are $a = 11{\cdot}07$ A, $b = 9{\cdot}03$ A, $c = 5{\cdot}09$ A, $\beta = 91{\cdot}8°$, $V = 508{\cdot}6$ A^3 and $Z = 2$. The calculated density is 1·619 g./cm.^{3} while that determined by the method of flotation is 1·64 g./cm.^{3}

Photographs for intensity estimation were taken using the multiple film technique and the intensities were estimated visually. After correction for the L-P and absorption factors, they were placed on an absolute scale by Wilson's method. The coefficient B in the isotropic temperature factor $\exp(-B \sin^4\theta/\lambda^2)$ was found to be 2·35 A^2 from the Wilson pot. However, it was found later that this value had to be altered appreciably, namely, from 2·35 to 3·00 A^2. As the compound was rather unstable the needles were enclosed in a quartz tube during exposure. However, the data for the [010] zone could be collected only at a later stage as it was difficult to enclose the crystal cut perpendicular to the needle axis inside the quartz tube. Finally the crystallite was dipped in a solution of cellulose acetate to obtain a thin film coated on it which prevented decomposition.

The atomic scattering factors of Viervoll and Ögrim (1949) were used in structure factor calculations.

The total number of reflexions theoretically accessible using Cu Kα radiation was 145 in the [001] zone and 152 in the [010] zone while the numbers experimentally accessible on the photographs were respectively 138 and 142. Of these 10 in the [001] zone and 12 in the [010] zone were observed to have zero intensity.

Refinement of the *b*-Axis Projection

In order to facilitate the discussions the following notation is used. The calculated structure factors usually denoted by F_c (hkl) is now replaced by $F^{(p)}$ (hkl) where the superscript p denotes that the structure factors have been calculated for a particular set (corresponding to the p-th stage of refinement) of co-ordinates listed in Tables I and II. The same symbol with a subscript H denotes that the calculated structure factors include hydrogen contributions. The same type of symbols have been used, where necessary, for denoting the reliability indices also. Thus, for example, $R_H^{(5)}$ ($h0l$) denotes the reliability index for the set of structure factors $F_H^{(5)}$ ($h0l$) which correspond to the 5th set of co-ordinates for this zone and include hydrogen contributions. If sets of structure factors are different due to reasons other than change in co-ordinate parameters of the atoms (as for example change in temperature factor, rescaling, etc.) they are denoted by $F_H^{(5a)}$ ($h0l$), $F_H^{(5b)}$ ($h0l$), etc. The observed structure amplitudes are denoted as usual, by F_o (hkl) and the indices hkl are dropped if there is no ambiguity.

Refinement of Chlorine Position

Since the present compound is isomorphous with the hydrobromide, a set of co-ordinates taken from a fairly advanced stage of refinement of the hydrobromide would provide us with a good approximation for starting the refinement. With regard to the co-ordinates of chlorine it would be necessary to choose the initial values as accurately as possible. The x co-ordinate was obtained from the position of the Cl—Cl peak in the c-axis Patterson projection. The x, z co-ordinates could have been similarly obtained from the b-axis Patterson projection, but, as mentioned earlier, the intensity data for this zone were not ready and therefore the corresponding Patterson map was not available. Now it was thought that instead of calculating the b-axis Patterson at a later stage to get the z co-ordinate of chlorine one could as well use the z co-ordinate of bromine as they would not be very much different from each other. Thus the x co-ordinate was found

to be 0·418 (from the *c*-axis Patterson) and z was assumed to be 0·437 which corresponded to the final refined value of bromine co-ordinates (Part I). The x and z co-ordinates of the light atom were taken from the hydrobromide at a stage when R (*h*0*l*) was 15·3 per cent.

These set of initial co-ordinates (Table I) gave $R^{(1)}$ (*h*0*l*) = 37 per cent. for the structure factors $F^{(1)}$ (*h*0*l*). The R value was rather large compared with that of 15·3 per cent. for the hydrobromide corresponding to the same light atom co-ordinates. The value was large even if we allowed for the fact that the hydrobromide was a compound containing a heavier atom. From this it could be inferred that either all the light atom positions were somewhat different from those assumed from the hydrobromide or that the co-ordinates of chlorine themselves might be appreciably different. The latter was thought more probable since the co-ordinate (z) of this atom was not obtained directly but was assumed to be same as that of bromine. In order to clarify the position a difference Fourier synthesis (Fig. 1) was computed using the structure factors $F^{(1)}$ (*h*0*l*). As expected, it showed a large slope at the position of chlorine, the shift indicated being mainly in the z direction. Though slopes at the positions of the other light atoms were also noticed, it was thought that it would be better to refine the position of chlorine first, since it was quite heavy and then take up the refinement of the light atoms.

The least squares formula,

$$\Delta x_i = \frac{\Sigma W^2 (F_o - F_c)\left(\frac{\partial F_c}{\partial x_i}\right)}{\Sigma W^2 \left(\frac{\partial F_c}{\partial x_i}\right)^2} \qquad (1)$$

was used to refine the x, z co-ordinates. In using the above formula the precautions mentioned in connection with the hydrobromide (Part I) were observed.

Three cycles of least squares refinement of the position of chlorine alone were carried out. The R values at these stages were respectively $R^{(2)}$ (*h*0*l*) = 33·6 per cent., $R^{(3)}$ (*h*0*l*) = 27·7 per cent. and $R^{(4)}$ (*h*0*l*) = 27·2 per cent. The total shifts in the z and x co-ordinates were respectively 0·16 Å and 0·06 Å. Since the refinement of the co-ordinates of chlorine seemed to have converged that of the light atoms was taken up.

TABLE I

L-Tyrosine hydrochloride: Co-ordinates at different stages of refinement of the [010] *projection*

Fractional z co-ordinates, (z/c)

Atom	p 1	2	3	4	5	6	7	8	9	10	11
C_1	0·363	..	..	..	0·352	0·373	0·357	..	0·364	0·362	..
C_2	0·151	..	..	..	0·160	0·160	0·160	..	0·157	..	..
C_3	0·035	..	..	..	0·033	0·028	0·029	..	0·019	..	..
C_4	0·087	..	..	..	0·076	0·100	0·090	..	0·082	..	0·088
C_5	0·293	..	..	..	0·296	0·296	0·302	..	0·304	..	..
C_6	0·437	..	..	..	0·447	0·443	0·445	..	0·445	..	..
C_7	0·938	..	..	..	0·905	0·925	0·938	..	0·928	..	0·922
C_8	0·070	..	..	..	.	..	0·055	..	0·072	..	0·075
C_9	0·170	..	..	..	..	..	0·138	..	0·148	0·154	0·155
O_1	0·533	..	..	..	0·514	0·522	0·519	..	0·519	..	0·520
O_2	0·010	..	..	..	..	..	0·008	..	0·003	..	..
O_3	0·371	..	..	..	0·377	0·377	0·372	..	0·372	..	0·373
N	0·931	..	..	..	0·919	0·919	0·912	..	0·912	..	..
Cl	0·437	0·426	0·412	0·405	..	..	..	..	..	..	..

Fractional x co-ordinates, (x/a)

Atom	p 1	2	3	4	5	6	7	8	9	10	11
C_1	0·094	..	..	..	0·097	0·097	0·098	..	0·102	0·100	0·098
C_2	0·081	..	..	..	0·080	0·080	0·083	..	0·083	..	..
C_3	0·980	..	..	..	0·974	0·979	0·977	..	0·975	..	..
C_4	0·881	..	..	..	0·881	0·883	0·879	..	0·874	0·877	0·879
C_5	0·898	..	..	..	0·900	0·905	0·900	..	0·902	..	0·897
C_6	0·998	..	..	..	0·009	0·006	0·003	..	0·006	..	..
C_7	0·757	..	..	..	0·759	0·759	0·763	..	0·761	..	..
C_8	0·660	..	..	..	..	..	0·667	0·657	0·657	..	0·656
C_9	0·670	..	..	..	..	..	0·658	0·663	0·663	0·665	0·667
O_1	0·196	..	..	..	0·195	0·204	0·200	..	0·200	..	0·202
O_2	0·635	..	..	..	..	..	0·626	0·635	0·635	..	0·640
O_3	0·736	..	..	..	0·720	0·730	0·726	..	0·727	..	0·723
N	0·545	..	..	..	0·530	0·539	0·538	..	0·542	..	..
Cl	0·418	0·415	0·414	0·413	..	..	..	..	..	..	..

TABLE II

Co-ordinates at different stages of refinement of the [001] *projection of L-tyrosine hydrochloride*

Atom	*p* 1	2	3	4	5	
C_1 ..	0·030	0·035	0·035	0·035	0·035	
C_2 ..	0·130	0·127	0·127	0·127	0·127	
C_3 ..	0·130	0·128	0·128	0·128	0·128	
C_4 ..	0·030	0·032	0·032	0·035	0·035	
C_5 ..	0·930	0·935	0·936	0·936	0·941	
C_6 ..	0·930	0·940	0·936	0·936	0·940	
C_7 ..	0·030	0·035	0·035	0·035	0·035	Fractional
C_8 ..	0·090	0·094	0·088	0·087	0·087	*y* co-ordinates,
C_9 ..	0·250	0·240	0·244	0·247	0·247	(*y*/*b*)
O_1 ..	0·030	0·032	0·034	0·034	0·034	
O_2 ..	0·345	0·349	0·354	0·354	0·353	
O_3 ..	0·275	0·278	0·282	0·278	0·273	
N ..	0·070	0·077	0·074	0·074	0·074	
Cl ..	0·250	..	..	..	..	
C_1 ..	0·098	0·100	0·100	0·100	0·100	
C_2 ..	0·083	0·082	0·080	0·080	0·080	
C_3 ..	0·977	0·974	0·971	0·971	0·971	
C_4 ..	0·879	0·877	0·877	0·876	0·878	
C_5 ..	0·900	0·896	0·896	0·897	0·897	
C_6 ..	0·003	0·008	0·010	0·010	0·010	
C_7 ..	0·763	0·765	0·767	0·763	0·763	Fractional
C_8 ..	0·667	0·663	0·657	0·654	0·651	*x* co-ordinates,
C_9 ..	0·658	0·662	0·663	0·665	0·671	(*x*/*a*)
O_1 ..	0·200	0·201	0·202	0·202	0·202	
O_2 ..	0·626	0·634	0·635	0·639	0·638	
O_3 ..	0·726	0·725	0·724	0·724	0·723	
N ..	0·538	0·535	0·538	0·538	0·538	
Cl ..	0·413	..	..	..	..	

Refinement of the Co-ordinates of the Light Atoms

The first cycle of least squares refinement of the light atoms was carried out and it gave considerable shifts in all the light atom co-ordinates (Table I). A significant feature noticed in this connection was that the z co-ordinate shifts in all the light atoms were more or less of the same magnitude and also for most of them the sense was the same. This indicated that the molecule had to be shifted as a whole from the initial assumed position. The maximum shifts were about 0·16 Å and 0·18 Å respectively in the z and x co-ordinates. These refined co-ordinates resulted in a reduction of the R value from $R^{(4)}$ $(h0l) = 27{\cdot}2$ per cent. to $R^{(5)}$ $(h0l) = 24{\cdot}5$ per cent.

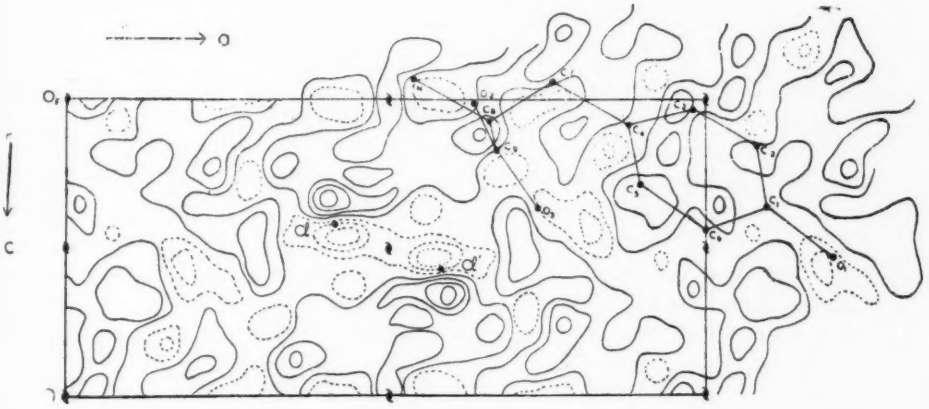

Fig. 1. The b-axis difference Fourier projection using the structure factors $F^{(1)}(h0l)$. Contours are at intervals of 0·5 e/A^2.

A second cycle of refinement of the light atoms was now gone through. The maximum shifts were found to be about 0·13 and 0·11 Å respectively in the z and x co-ordinates. The structure factors $F^{(6)}$ $(h0l)$ were now calculated and the value of $R^{(6)}$ $(h0l)$ was found to be 22·8 per cent.

In both the above stages of light atom refinement the overlapping group of atoms C_8, C_9 and O_2 was not included but was reserved for a later stage.

Approximate positions of hydrogen atoms were now fixed up from bond length considerations. When these were included in the calculation of the structure factors, the R value obtained was $R_H^{(6)}$ $(h0l) = 21{\cdot}9$ per cent.

Since the convergence seemed to have slowed down it was now decided to include the low angle reflexions also in the refinement. This would be

possible now since the hydrogen contributions had also been included. The overlapping group of atoms C_8, C_9, O_2 was also now included in this third cycle of refinement.

The method of treating the overlapping group was the same as that described for the hydrobromide compound (Part I). The sixth order normal equations of least squares involving the x and y parameter shifts of the three atoms C_8, C_9 and O_3 were formed and were solved by the Gauss-Seidel iterative method (Whittaker and Robinson, 1945). The light atoms were also refined as usual and the new set of co-ordinates was used to calculate the structure factors $F^{(7)}$ ($h0l$). In spite of the fact that some of the shifts were quite considerable the value of R rather surprisingly remained stationary at $R^{(7)}$ ($h0l$) = 23 per cent.

It was now noticed that at high angles the calculated structure factors were systematically larger than the observed ones which indicated that the temperature factor needed alteration. Till now, only an isotropic temperature factor with $B = 2{\cdot}35$ Å^2 had been used. Since the refinement seemed to have reached a fairly advanced stage the structure factors $F^{(7)}$ ($h0l$) were used along with the values of $|F_o|$ in plotting the usual graph of $\log\{\langle|F_c|\rangle/\langle|F_o|\rangle\}$ against $(\sin^2\theta/\lambda^2)$. The graph gave a value of $3{\cdot}00$ A^2 for B. The scale factor was also found to be altered slightly and when these were introduced into the new calculations the R values were found to be $R^{(7a)}$ ($h0l$) = $22{\cdot}3$ per cent. and $R_H{}^{(7a)}$ ($h0l$) = $20{\cdot}5$ per cent.

It might be remembered that the refinement of chlorine had been stopped (after three cycles of least squares refinement) at a stage when R value was $27{\cdot}2$ per cent. The fourth cycle of refinement of chlorine alone was now carried out using the structure factors $F_H{}^{(7a)}$ ($h0l$). The shifts obtained were quite negligible, namely, $0{\cdot}005$ Å and $0{\cdot}001$ Å respectively in the z and x co-ordinates. The refinement of chlorine position was therefore assumed to be complete. As the shifts were negligible no new calculations were made with the new co-ordinates of chlorine.

It was now thought that, since the atoms C_8, C_9 and O_2 were fairly well resolved in the other c-axis projection it would be better to use, for these atoms alone, the values of x refined from that projection. The refinement of the c-axis projection had actually reached a well advanced stage after two cycles of least squares refinement, the R values then being $R^{(3)}$ ($hk0$) = $18{\cdot}2$ per cent. and $R_H{}^{(3)}$ ($hk0$) = $16{\cdot}8$ per cent. (*see* next section). The x co-ordinates of C_8, C_9 and O_2 were thus assumed to be those used in the calculation of $F^{(3)}$ ($hk0$). All other co-ordinates were the same as those used

for $F^{(7)}$ $(h0l)$. The new calculation gave R^8 $(h0l) = 21{\cdot}0$ per cent. and R_H^8 $(h0l) = 19{\cdot}2$ per cent. The improvement in the R value for the structure factors $F^{(8)}$ $(h0l)$ as compared with $F^{(7)}$ $(h0l)$ showed that the x co-ordinates of C_8, C_9 and O_2 were now definitely more accurate than those used for $F^{(7)}$ $(h0l)$.

However, even now the R value seemed to be rather large (21 per cent.). But one striking fact was that the inclusion of hydrogen contribution improved the R value nearly by 2·0 per cent. This seemed to be due to the use of the structure factors F_H $(h0l)$ for refinement. It also points to the importance of including hydrogen contributions at quite an early stage of refinement. The above situation may be compared with that in the hydrobromide (Part I) when even at the final stage of refinement (R $\simeq$ 12 per cent.) the inclusion of hydrogen contribution practically left the R value unaffected.

The rather large value of R (19·2 per cent.) was actually found to be due to the presence of extinction effect in some of the reflexions. The graphical method of correction (Part I) was adopted and the value of G was found to be $0{\cdot}15 \times 10^{-3}$. The value of G was used to correct the observed structure amplitude and it resulted in $R_H^{(8a)}$ $(h0l) = 16{\cdot}0$ per cent.

A fourth cycle of least squares refinement of the light atoms including the overlapping group was now gone through. However, while solving the simultaneous equations of the overlapping group the shifts in the x co-ordinates of C_8, C_9 and O_2 were assumed to be zero and this was because the refined values from the other projection were used in the calculations. The new calculations gave practically a stationary value of $R_H^{(9)}$ $(h0l) = 16{\cdot}0$ per cent.

Difference Fourier Syntheses and Temperature Factor Refinement

A difference Fourier synthesis (Fig. 2) was now computed using the structure factors $F_H^{(9)}$ $(h0l)$. The reason for using the structure factors which included the hydrogen contributions was that the synthesis was intended for a study of anisotropy of thermal vibrations of the atoms. The synthesis proved to be really useful. The main features of the map were the following:

(1) There was a marked anisotropy in the vibration of the chlorine atom.

(2) A similar anisotropy was noticed for the light atoms also, more especially for the oxygens.

(3) The shapes of the positive and negative peaks indicated that the directions of vibration of the light atoms were more or less the same as that of chlorine.

(4) The slopes at the positions of some of the light atoms had not vanished indicating thereby that those co-ordinates needed shifting.

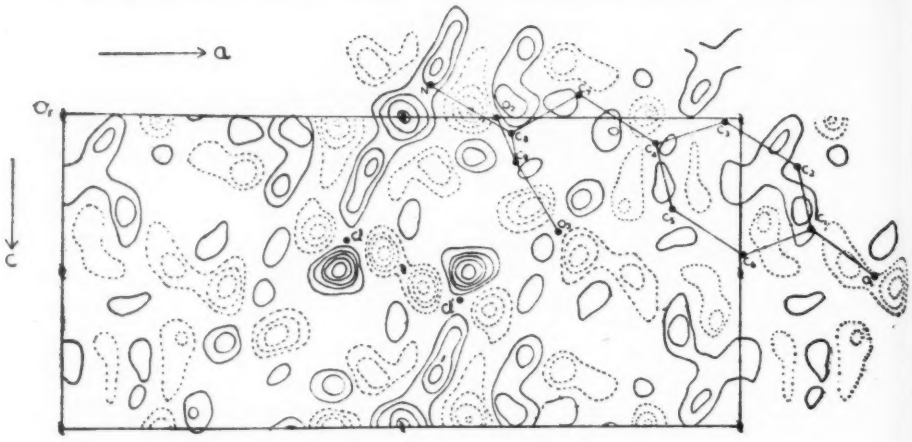

FIG. 2. The *b*-axis difference Fourier projection using the structure factors $F_o^{(9)}(h0l)$. Contours are at intervals of $0{\cdot}2\ e/A^2$.

The third of the features mentioned above seems to be rather significant. The fact that the directions of vibration of the different atoms are almost the same indicates that the whole process can be approximated to one of vibration of the molecule as a whole. This goes to justify at least partially the view (Wells, 1956) that an overall anisotropic temperature factor could be applied for a particular reflexion. Moreover the assumption of anisotropic parameters for individual atoms and their refinement demands an abundance of data which could be had only if they are collected three dimensionally. Therefore only the overall anisotropic thermal parameters B_{11}, B_{12}, etc., were assumed so that we could write.

$$F_c\,(hkl) = F_c'\,(hkl)\,\exp\text{-}(B_{11}\,h^2 + B_{22}\,k^2 + B_{33}\,l^2 + B_{13}hl) \qquad (2)$$

where $F_c'\,(hkl)$ is the calculated structure factor without applying the temperature factor. The parameters B_{11}, B_{12}, etc., were now refined by the method of least squares. The initial starting values of B_{11}, B_{12}, etc., were obtained from the isotropic temperature factor with $B = 3{\cdot}0\ Å^2$ (*see* Part I).

However, just for the sake of interest the anisotropic thermal parameters b_{11}, b_{33} and b_{13} for chlorine alone were refined from this *b*-axis projection. Surprisingly the value of b_{11}, b_{33} and b_{13} obtained for chlorine agreed closely with the overall thermal parameters B_{11}, B_{33} and B_{13} (Table III). This,

of course, may be explained as being due to the fact that chlorine, being rather heavy, contributes predominantly to the structure factors. However, the individual anisotropic parameters for chlorine were never used in the calculations but only the overall parameters were used.

TABLE III

L-tyrosine hydrochloride : Overall anisotropic thermal parameters obtained by the method of least squares

Zone*	$(A)^2$			
	B_{11}	B_{22}	B_{33}	B_{13}
[001]	0·0052	0·00954	..	..
[010]	0·0050	..	0·0344	− 0·00370
Value from isotropic $B = 3·0\ A^2$	0·00617	0·00919	0·0300	− 0·00033
Value for chlorine	0·00320	..	0·0332	− 0·00350

* The anisotropic thermal parameters for chlorine alone were obtained by the method of least squares for the (010) zone. However these values were not used in calculations.

Before applying the anisotropic temperature factor it was thought that the difference map itself could be used to obtain the shifts in the various co-ordinates. The formula

$$\Delta x_i = \frac{-\left[\frac{\partial(\rho_o - \rho_c)}{\partial x}\right]_i}{\left(\frac{\partial^2 \rho_o}{\partial x^2}\right)_i} \qquad (3)$$

was used for this purpose. The usual approximation of $\partial^2\rho_o/\partial x^2 = 2p\rho_o$ was made and the values of p for different atoms were obtained graphically using the electron density distribution near the peaks (Part I). The values were $p = 2·65$, 2·8, 3·0 and 4·3 respectively for C, N, O and Cl.

The new co-ordinates thus obtained were used in the calculation of the structure factors $F^{(10)}$ $(h0l)$. However, to see how these new co-ordinates alone affected the R value the original isotropic temperature factor with $B = 3·0\ A^2$ was applied to the structure factors $F^{(10)}$ $(h0l)$ and the values of the reliability indices were $R^{(10)}$ $(h0l) = 17·7$ per cent. and $R_H{}^{(10)}$ $(h0l) = 15·8$ per cent. When the overall anisotropic factor was applied the values were $R^{(10a)}$ $(h0l) = 16·4$ per cent. and $R_H{}^{(10a)}$ $(h0l) = 14·4$ per cent.

The fact that the inclusion of hydrogen contributions improved the R value nearly by 2 per cent. indicated that the difference Fourier could now be employed to locate these atoms. Accordingly a difference Fourier using $F^{(10a)}$ $(h0l)$ was computed (Fig. 3). As expected, it showed peaks at assumed positions of hydrogens. The map also showed that the anisotropy had been practically corrected for, since the characteristic positive and negative peaks

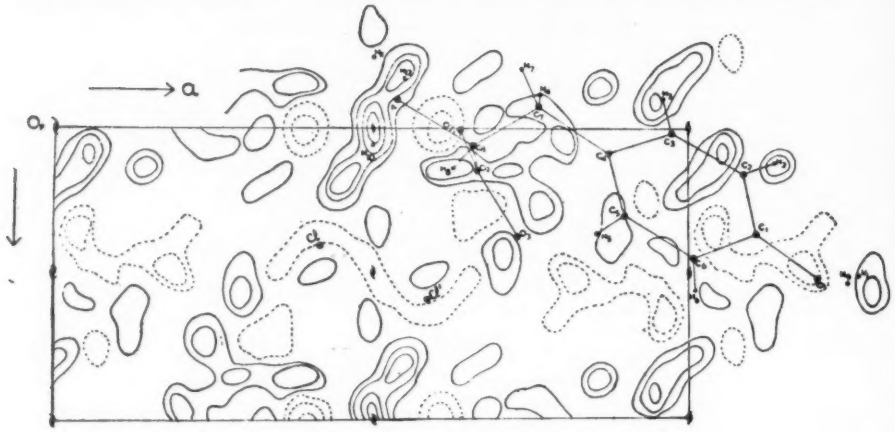

FIG. 3. The *b*-axis difference Fourier projection using the structure factors $F^{(10a)}$ $(h0l)$. The assumed positions of hydrogen atoms (Table V) have been marked. Contours are at intervals of 0·2 e/A^2.

had almost completely vanished. The map gave slight shifts in some of the light atom co-ordinates. The new set of calculations gave almost stationary values of R^{11} $(h0l) = 16{\cdot}2$ per cent. and $R_H{}^{(11)}$ $(h0l) = 14{\cdot}3$ per cent. The refinement of this projection was now assumed to be complete. The values of R when reflexions with $|F_o| = 0$ are omitted are: R $(h0l) = 14{\cdot}5$ per cent. and R_H $(h0l) = 13{\cdot}0$ per cent.

REFINEMENT OF THE *c*-AXIS PROJECTION

In order to reduce the total work involved in this non-centrosymmetric projection it was decided to start the refinement with a fairly close approximation to the real co-ordinates. This was possible since the refinement of the other projection had been started earlier and had reached a fairly well advanced stage. The x co-ordinates of the light atoms were now assumed to be those used in the calculation of the structure factors $F^{(7)}$ $(h0l)$. The y co-ordinates were chosen from bond length considerations. This set of initial x, y co-ordinates (Table II) was used to calculate the structure factors

$F^{(1)}$ ($hk0$). As mentioned in the last section the structure factors $F^{(7)}$ ($h0l$) had been used along with the values of $|F_o|$ to obtain more accurate scale and temperature factors. A similar graphical procedure was now adopted for this c-axis projection also. The value of $B = 3{\cdot}0\ A^2$ was obtained from the graph and this was indentical with the value obtained from the other projection.

Using this isotropic temperature factor the R value was found to be $R^{(1)}$ ($hk0$) = 23·0 per cent.

The least squares refinement of both x and y co-ordinates from this projection was now started. For the refinement of the y co-ordinates from this non-centrosymmetric projection the formula is the same as that given by equations (8) and (9) of Part I. However, for the refinement of the x co-ordinates, which was not carried out in the case of the hydrobromide, we have to use the more general expression

$$\Delta x_i = \frac{\sum_{h,k} W^2 \left(\frac{|F_o| - |F_c|}{|F_c|}\right) \left\{A \frac{\partial A}{\partial x_i} + B \frac{\partial B}{\partial x_i}\right\}}{\sum \left(\frac{W^2}{I_c}\right) \left\{A \frac{\partial A}{\partial x_i} + B \frac{\partial B}{\partial x_i}\right\}^2} \tag{6}$$

where, for k even,

$$\left(\frac{\partial A}{\partial x_i}\right) = 4\pi h f_i \cos 2\pi k y_i \sin 2\pi h x_i$$

$$\left(\frac{\partial B}{\partial x_i}\right) = -\,4\pi h f_i \sin 2\pi k y_i \sin 2\pi h x_i$$

and for k odd (7)

$$\left(\frac{\partial A}{\partial x_i}\right) = -\,4\pi h f_i \sin 2\pi k y_i \cos 2\pi h x_i$$

$$\left(\frac{\partial B}{\partial x_i}\right) = 4\pi h f_i \cos 2\pi k y_i \cos 2\pi h x_i$$

The refinement of y co-ordinates is thus easier since the quantities A, A_i, B, B_i in (4) would already have been prepared during structure factor calculations while, for the refinement of the x co-ordinates, the quantities $(\partial A/\partial x_i)$, $(\partial B/\partial x_i)$ in (6) have to be calculated afresh using (7).

The set of x, y co-ordinates obtained from the first cycle of least squares refinement was used to calculate the structure factors $F^{(2)}$ ($hk0$) and it

resulted in $R^{(2)}$ $(hk0) = 19{\cdot}0$ per cent. When hydrogen contributions were now included, it gave $R_H{}^{(2)}$ $(hk0) = 18{\cdot}4$ per cent. A second cycle of least squares refinement now reduced the R value to $F^{(3)}$ $(hk0) = 18{\cdot}2$ per cent. and $R_H{}^{(3)}$ $(hk0) = 16{\cdot}8$ per cent.

Some of the reflexions which showed extinction effects were now corrected for by the graphical method mentioned already. The value of G was found to be $0{\cdot}2\times10^{-3}$. After extinction correction the R values were $R^{(3a)}$ $(hk0) = 15{\cdot}4$ per cent. and $R_H{}^{(3a)}$ $(hk0) = 13{\cdot}6$ per cent.

Difference Fourier Syntheses and Temperature Factor Refinement

A difference Fourier synthesis (Fig. 4) was now computed to study the general anisotropy of thermal vibrations. The map showed anisotropy for chlorine and also for some of the light atoms. This, of course, was expected

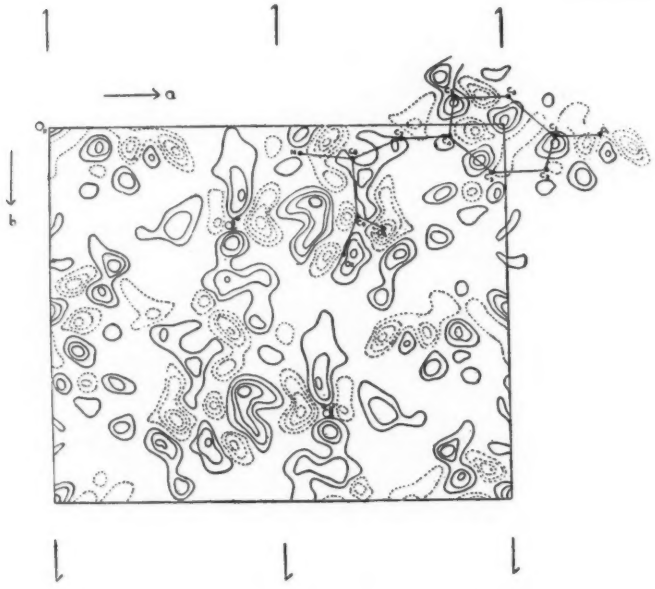

FIG. 4. The *c*-axis difference Fourier projection using the structure factors $F^{(3a)}$ $(hk0)$. Contours are at intervals of $0{\cdot}2\ e/A^2$.

since a difference Fourier of the other projection at a corresponding stage also showed similar features. In this *c*-axis projection also the general nature of the vibrations of the light atoms and of the chlorine atoms were quite

similar. Co-ordinate shifts were also obtained by the usual method. However, the use of the new co-ordinates left the R values practically unaltered at $R^{(4)}$ $(hk0) = 15{\cdot}3$ per cent. and $R_H{}^{(4)}$ $(hk0) = 13{\cdot}8$ per cent. Only isotropic temperature factor with $B = 3{\cdot}0\ A^2$ was used in the above calculation.

The refinement of the overall anisotropic factor was then carried out. For this projection, the appropriate form of the factor was $\exp-(B_{11}h^2 + B_{22}k^2)$. The initial values were obtained as usual from the isotropic value, $B = 3{\cdot}0\ A^2$. The value of B_{11} refined from this projection agreed well with that from the other projection (Table III). Application of the overall temperature factor gave $R^{(4a)}$ $(hk0) = 14{\cdot}4$ per cent. and $R_H{}^{(4a)}$ $(hk0) = 13{\cdot}1$ per cent.

It could be noticed that, in this projection also, the inclusion of hydrogen contribution improved the R value nearly by 1·3 per cent. Therefore, with the object of locating the hydrogen positions, a difference Fourier was computed (Fig. 5) using $F^{(4a)}$ $(hk0)$. However, probably because this projection

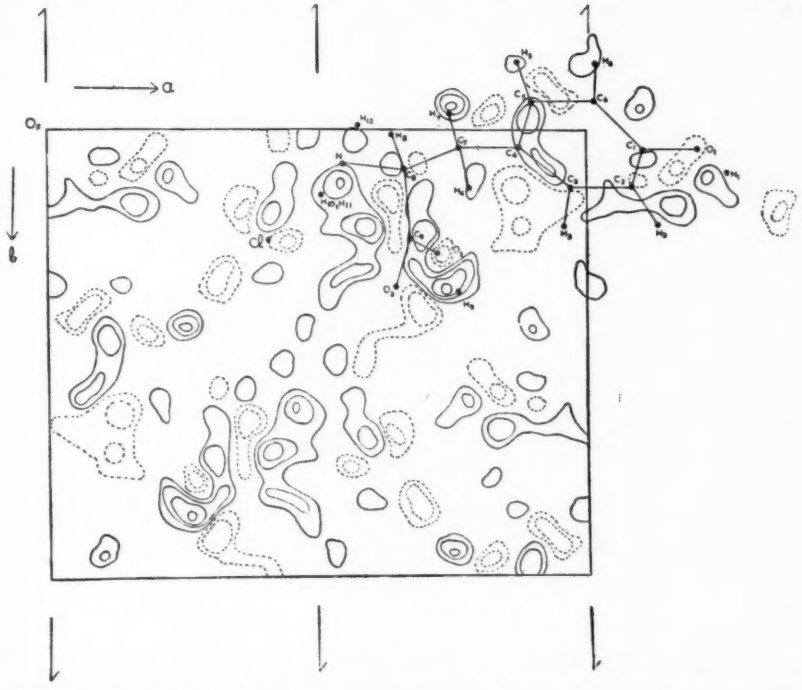

FIG. 5. The *c*-axis difference Fourier projection using the structure factors $F^{(4a)}$ $(hk0)$. Contours are at intervals of $0{\cdot}2\ e/A^2$.

was non-centrosymmetric, the map was not as good as that of the *b*-axis projection. Yet, faint maxima were discernible at the positions of hydrogen atoms. The anisotropy was also found to have practically vanished. Shifts in the co-ordinates of some of the atoms were also obtained. The new calculation gave $R^{(5)}$ $(hk0) = 14{\cdot}1$ per cent. and $R_H{}^{(5)}$ $(hk0) = 12{\cdot}9$ per cent. The almost stationary value of R was taken as an indication of the convergence of the refinement process which was therefore stopped. The co-ordinates at different stages of refinement of this projection are listed in Table II.

It was now noticed that two reflexions in this zone namely, 230 and 330, had rather large discrepancies between their calculated and observed structure amplitudes. A careful examination showed that both of them occurred at low angles and also for both of them $|F_c|$ was greater than $|F_o|$. This showed that the effects of extinction were present in them. The reason why they had been left out during the previous graphical correction was found to be the following. In order to look for the reflexions that suffer from extinction we have to take the intensities which are not corrected for L-P factors, and

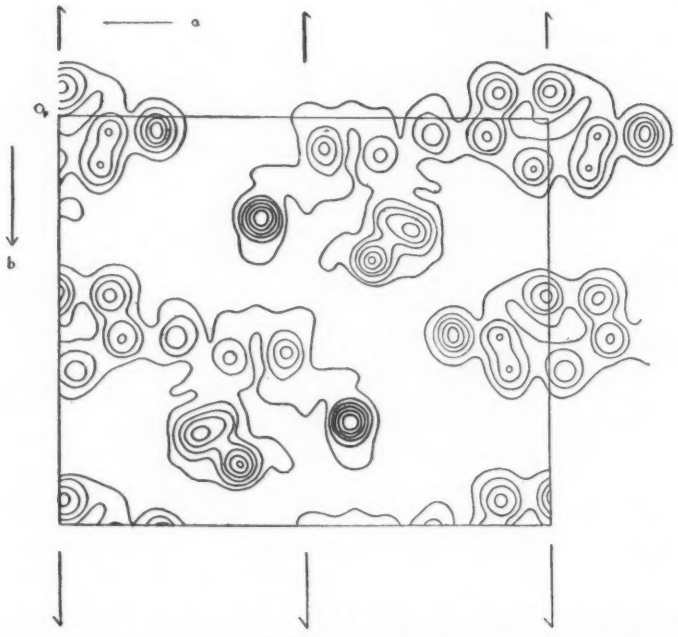

FIG. 6. The final *c*-axis Fourier projection of L-tyrosine hydrochloride. Contours are at intervals of 1 e/A^2, starting from $2{\cdot}0$ e/A^2. For chlorine the interval is $2{\cdot}0$ e/A^2.

not the intensities as judged from the tables of structure factors, $|F_o|$ and $|F_c|$. While the values might not be large if taken from tables of $|F_o|$ and $|F_c|$ they might be quite large when L-P factors are taken into account. This was actually found to be the case with the reflexions 230 and 330. These reflexions also fitted well into the extinction graph and the original value of G could now be retained and applied to these reflextions also. This gave the values of $R^{(5a)}$ $(hk0) = 13{\cdot}45$ per cent. and $R_H{}^{(5a)}$ $(hk0) = 12{\cdot}25$ per cent. When reflexions with $|F_o| = 0$ were omitted the values were: $R\,(hk0) = 11{\cdot}5$ per cent. and $R_H\,(hk0) = 10{\cdot}3$ per cent. Thus the final R values in percentage are,

		With hydrogens	Without hydrogens
R (*h*0*l*)	All reflexions	14·3	16·2
	$\|F_o\| = 0$, omitted	13·0	14·5
R (*hk*0)	All reflexions	12·25	13·45
	$\|F_o\| = 0$, omitted	10·30	11·50

The final set of accepted co-ordinates is given in Table IV. The assumed co-ordinates of hydrogen atoms are listed in Table V. The calculated and observed structure factors are given in Tables VI and VII. The final Fourier syntheses are shown in Figs. 6 and 7.

Accuracy of the Structure Determination

The standard deviations in the co-ordinates and in other parameters were calculated on the same lines as described in Part I. The values obtained are listed in Table VIII. The two values obtained for the standard deviation in the x co-ordinate which is common to both the projections agreed closely and only the average is given in Table VIII. It can be seen from the table that the standard errors in the different x, y, z co-ordinates for any particular atom are almost the same, so that an average value can be taken. Using these values, the standard errors in the various bond distances are found to be

$$C—C = 0{\cdot}033\ \text{Å},\quad C—N = 0{\cdot}029\ \text{Å},\quad C—O = 0{\cdot}027\ \text{Å}$$

and

$$O—O = 0{\cdot}021\ \text{Å}.$$

The standard error in electron density is about $0{\cdot}2\ e/\text{Å}^2$ while that in a typical angle in the benzene ring is about 2·3°. All the probable errors have to be taken as slightly larger for the overlapping group of atoms C_8, C_9 and O_2.

TABLE IV

Final accepted co-ordinates in L-tyrosine hydrochloride

Atom	x/a*	y/b	z/c	x (A)	y (A)	z (A)
C_1 ..	0·0990	0·035	0·362	1·096	0·316	1·843
C_2 ..	0·0815	0·127	0·157	0·902	1·147	0·799
C_3 ..	0·9730	0·128	0·019	10·771	1·156	0·097
C_4 ..	0·8785	0·033	0·088	9·725	0·316	0·448
C_5 ..	0·8970	0·941	0·304	9·930	8·497	1·547
C_6 ..	0·0080	0·940	0·445	0·089	8·488	2·265
C_7 ..	0·7620	0·035	0·922	8·435	0·316	4·693
C_8 ..	0·6530	0·087	0·075	7·229	0·786	0·382
C_9 ..	0·6690	0·247	0·155	7·406	2·230	0·789
O_1 ..	0·2020	0·034	0·520	2·236	0·307	2·647
O_2 ..	0·6390	0·353	0·003	7·074	3·188	0·015
O_3 ..	0·7230	0·273	0·373	8·004	2·465	1·899
N ..	0·5400	0·074	0·912	5·978	0·668	4·642
Cl ..	0·4130	0·250	0·405	4·572	2·258	2·061

* Average value from the two projections (Tables I and II).

It is to be noted that the x co-ordinates refined from the two projections agree closely within the limits of the estimated errors. The final table of co-ordinates contains only the average value.

It can be noticed that the final R values of the two projections are considerably different, namely, R_H ($h0l$) = 13·0 per cent. and R_H ($hk0$) = 10·3 per cent. The difference can be attributed to the fact that the R value in a non-centrosymmetric case is smaller than that in a centrosymmetric case. The statistical treatment of the problem (Luzzati, 1952) also indicates this result. Although Luzzati's results are not strictly valid at the final stages of refinement and also for compounds containing unequal atoms, we can at

least take his results to be broadly true. The difference in the R values can be thought of as arising from the fact that, when the assumed structure is different from the correct one, only the differences in the modulii ($|F_o| - |F_c|$) can occur in a non-centrosymmetric structure while the vector

TABLE V

Assumed positions of hydrogen atoms in L-tyrosine hydrochloride*

Atom		x/a	y/b	z/c
H_1 (O_1)	..	0·26	0·10	0·51
H_2 (C_2)	..	0·13	0·21	0·12
H_3 (C_3)	..	0·96	0·21	0·90
H_4 (C_7)	..	0·77	0·13	0·88
H_5 (C_5)	..	0·86	0·84	0·36
H_6 (C_6)	..	0·01	0·84	0·56
H_7 (C_7)	..	0·74	0·97	0·80
H_8 (C_8)	..	0·63	0·01	0·13
H_9 (O_3)	..	0·75	0·36	0·46
H_{10} (N)	..	0·50	0·15	0·05
H_{11} (N)	..	0·50	0·15	0·73
H_{12} (N)	..	0·56	0·99	0·82

* (1) The positions of these hydrogen atoms are almost the same as in L-tyrosine hydrobromide.

(2) The position of H_{12} given in this table was the one used in calculations and was originally assumed to form the bond N (M) H .... Cl_{001}. However, it has since been assumed to form the bond N (M) H .... O_2 (M_{101}). No new calculations were made with this change in the position of this hydrogen.

difference ($F_o - F_c$) occur in a centrosymmetric case. In the latter one it is obviously possible to have a finite $|F_o - F_c|$ while $|F_o| - |F_c| = 0$. Hence the observed mean value of $\big||F_o| - |F_c|\big|$ will be less for a non-centrosymmetric than for a centrosymmetric case.

TABLE VI

Observed and calculated structure factors for the h0l *reflexions of L-tyrosine hydrochloride*

	F	F	F_H		F	F	F_H
	Observed	Calculated			Observed	Calculated	
*h*00				*h*02			
1	3·0	− 1·4	− 2·0	4	1·9	− 2·2	− 0·9
2	9·8	8·4	8·9	5	5·0	8·5	7·6
3	16·9	19·1	17·3	6	12·2	11·9	12·3
4	12·0	−12·7	− 9·0	7	5·5	− 5·0	− 4·9
5	9·8	9·9	9·5	8	9·4	9·9	9·9
6	16·1	−14·9	−15·0	9	7·4	− 3·1	− 3·5
7	2·2	2·3	2·5	10	13·3	13·2	12·7
8	5·0	2·8	4·8	11	4·0	− 2·4	− 2·2
9	11·6	12·3	12·1	12	0·0	− 1·1	− 0·9
10	8·3	8·0	7·5	13	2·9	3·3	3·3
11	1·8	2·6	2·3				
12	6·9	6·9	7·1	*h*03			
13	6·4	− 7·1	− 7·3				
				0	7·4	8·1	6·5
				1	4·4	− 5·7	− 5·4
*h*01				2	10·0	11·3	11·8
				3	11·7	−12·5	−13·4
0	6·6	1·7	3·2	4	10·9	9·2	8·6
1	2·5	3·1	− 0·6	5	17·6	−15·7	−16·1
2	9·0	6·7	8·5	6	7·1	− 5·0	− 4·4
3	10·6	− 6·0	− 6·7	7	10·8	11·9	10·5
4	12·0	−10·7	10·1	8	4·1	2·4	2·3
5	33·7	−32·6	−34·9	9	4·4	4·9	4·8
6	18·5	14·2	14·9	10	4·8	− 4·4	− 4·2
7	15·6	−11·5	−12·4	11	3·2	3·5	3·1
8	4·1	4·8	4·6	12	3·4	2·2	2·4
9	14·4	14·0	13·9				
10	19·4	−20·3	−20·5	*h*04			
11	6·2	6·3	6·1				
12	1·9	− 1·4	− 1·8	0	10·6	−10·0	−10·3
13	0·0	0·4	0·3	1	9·2	9·4	9·0
14	3·9	− 4·8	− 4·7	2	3·3	− 3·0	− 3·1
				3	14·3	12·0	12·0
				4	5·4	5·9	6·3
*h*02				5	5·4	4·4	4·0
				6	10·6	11·3	11·0
0	42·5*	38·1	38·9	7	11·6	−12·7	−12·8
1	8·3	− 5·6	− 6·8	8	6·0	7·3	7·3
2	19·2	−15·4	−17·9	9	4·0	− 3·7	− 4·0
3	30·4	33·3	34·2	10	3·2	1·2	1·4

TABLE VI—*Contd.*

	F Observed	F Calculated	F_H Calculated
*h*05			
0	3·3	3·8	3·6
1	5·5	− 5·7	− 5·7
2	9·9	9·2	9·3
3	11·6	10·0	9·8
4	1·9	− 2·4	− 2·5
5	2·9	4·4	4·7
6	2·4	− 2·0	− 2·0
7	4·4	4·3	4·4
8	4·1	− 3·8	− 4·0
9	3·5	− 6·1	− 6·2
*h*06			
0	3·2	− 2·3	− 2·3
1	2·6	2·9	2·9
2	1·2	− 2·5	− 2·5
3	0·0	− 1·2	− 1·2
4	1·9	2·5	2·5
$\bar{h}$01			
0	6·6	1·7	3·2
1	12·4	−11·9	−12·5
2	1·2	− 0·9	1·3
3	32·5*	34·3	32·7
4	23·8	−25·7	−27·0
5	4·3	− 3·3	− 1·7
6	20·5	21·3	21·3
7	19·3	−20·9	−21·8
8	10·0	10·5	10·3
9	2·4	− 0·2	− 0·3
10	15·8	−14·1	−13·7
11	0·3	1·5	1·1
12	9·0	− 8·5	− 8·7
13	5·0	6·2	6·0
$\bar{h}$02			
0	42·5	38·1	38·9
1	8·3	− 9·8	− 6·2
2	17·9	16·0	17·5
3	15·5	18·6	−17·9
4	8·3	7·3	7·8
5	33·5*	32·0	33·3
6	0·0	− 0·7	− 1·3
7	5·0	2·7	2·7
8	4·2	− 3·8	− 3·1
9	9·1	8·6	9·0
10	11·6	−12·1	−11·7
11	0·0	1·1	1·0
12	0·0	− 0·8	− 0·8
13	7·3	− 6·8	− 6·8
$\bar{h}$03			
0	7·4	8·1	6·5
1	0·0	− 2·0	− 2·4
2	4·5	− 5·8	− 4·3
3	18·5	22·8	22·5
4	15·8	−18·4	−18·9
5	8·5	8·9	8·4
6	5·3	− 5·2	− 4·5
7	5·6	− 2·7	− 2·7
8	9·2	9·2	9·0
9	9·0	− 8·5	− 8·7
10	2·9	2·4	2·8
11	0·0	− 0·3	− 0·4
12	2·4	− 3·4	− 3·5
$\bar{h}$04			
0	10·5	−10·0	−10·3
1	0·0	2·6	2·3
2	0·0	− 0·1	0·0
3	11·3	−10·5	−10·6
4	4·2	1·2	2·0
5	7·4	6·0	5·8
6	8·9	9·8	10·0
7	0·0	− 1·2	− 1·2
8	2·9	− 2·8	− 2·7
9	4·0	3·0	3·1

TABLE VI—*Contd.*

	F Observed	F Calculated	F_H Calculated		F Observed	F Calculated	F_H Calculated
$\bar{h}05$				$\bar{h}06$			
0	3·3	3·8	3·6	0	3·2	− 2·3	− 2·3
1	3·3	− 4·6	− 4·7	1	5·3	5·5	5·5
2	2·1	− 1·2	− 1·2	2	1·4	− 1·1	− 1·4
3	2·1	3·1	3·3	3	4·0	3·6	3·5
4	2·1	− 3·6	− 3·6	4	0·0	− 1·7	− 1·7
5	6·3	6·3	6·1	5	2·9	− 2·6	− 2·6
6	2·7	− 4·4	− 4·4				
7	4·0	4·2	4·4				
8	1·4	1·6	1·5				
9	1·9	− 2·2	− 2·2				

* These reflexions have been corrected for extinction effects.

TABLE VII

Observed and calculated structure amplitudes and calculated phase angles† for the hk0 *reflexions of L-tyrosine hydrochloride*

	$\lvert F_o \rvert$	$\lvert F \rvert$ Calculated	$\lvert F_H \rvert$ Calculated	α^0 Calculated		$\lvert F_o \rvert$	$\lvert F \rvert$ Calculated	$\lvert F_H \rvert$ Calculated	$\lvert \alpha^0 \rvert$ Calculated
*h*10					*h*30				
0	..	..	..	..	0	..	..	..	..
1	17·6*	17·8	18·3	345	1	14·6	11·9	13·5	270
2	14·5	12·7	15·5	149	2	31·4*	34·1	34·5	160
3	32·7*	32·5	33·4	196	3	26·2*	29·0	29·1	352
4	24·9	29·2	29·2	3	4	22·4*	24·6	25·4	199
5	9·1	11·1	9·0	213	5	6·5	6·8	6·1	32
6	14·7	13·6	13·7	99	6	8·6	9·7	9·5	36
7	16·6	14·5	14·4	359	7	9·2	9·1	9·8	100
8	11·3	8·4	9·0	170	8	11·2	10·3	10·0	18
9	22·0	22·7	23·0	334	9	6·4	6·9	6·8	316
10	7·6	7·9	8·0	227	10	8·6	9·9	9·8	21
11	2·3	2·4	2·6	30	11	4·4	4·0	4·3	115
12	5·4	5·5	5·5	22	12	2·8	2·8	2·8	158
13	5·0	5·0	4·6	196					
14	3·2	3·4	3·4	11					

† The phase angles correspond to F_H.

	$\|F_0\|$	$\|F\|$	$\|F_H\|$	$\|\alpha^0\|$		$\|F_0\|$	$\|F\|$	$\|F_H\|$	$\|\alpha^0\|$
		Calculated					Calculated		
*h*50					*h*11,0				
0	..	..	..	..	0	..	..	..	..
1	10·7	9·8	9·6	134	1	2·8	2·5	2·5	283
2	9·4	8·4	8·4	340	2	3·7	2·5	2·5	129
3	15·9	19·5	18·6	184	3	3·2	2·9	2·9	355
4	12·3	14·0	14·5	358					
5	0·0	2·7	1·4	90					
6	10·4	11·7	11·6	185	*h*20				
7	8·8	8·7	8·7	26					
8	5·0	6·0	6·0	189	0	22·0	23·7	26·0	77
9	9·0	10·0	9·8	8	1	50·0*	49·8	45·6	7
10	3·7	4·0	4·0	200	2	10·0	8·1	8·9	95
11	3·5	3·1	3·1	137	3	29·8*	31·0	30·4	210
12	3·2	4·2	4·2	126	4	12·0	11·2	12·0	43
					5	11·3	8·8	9·0	207
*h*70					6	10·7	14·3	12·4	345
					7	16·7	16·7	17·0	198
0	..	..	..	..	8	11·3	10·0	9·9	319
1	6·0	4·2	3·8	105	9	14·3	14·0	14·0	13
2	7·2	7·6	7·6	202	10	0·0	2·2	2·2	244
3	9·9	13·0	12·8	39	11	10·4	8·3	8·5	346
4	9·3	8·8	8·7	182	12	8·8	7·6	7·6	184
5	5·6	6·4	6·2	315	13	5·0	4·2	4·0	4
6	0·0	0·4	0·8	62					
7	7·2	8·3	8·2	185					
8	11·4	12·0	11·8	308	*h*40				
9	0·0	2·5	2·5	178					
10	5·7	4·4	4·4	325	0	29·7*	36·3	35·0	48
					1	17·2	17·5	17·0	225
*h*90					2	19·1	19·0	19·3	229
					3	10·5	11·2	9·7	218
0	..	..	..	..	4	4·2	2·0	3·8	202
1	2·5	2·9	2·9	136	5	8·1	7·2	7·3	351
2	3·6	3·9	4·0	29	6	14·6	15·9	15·9	186
3	7·9	7·9	7·9	183	7	15·0	15·3	15·5	337
4	6·8	7·5	7·5	3	8	00·0	4·0	4·4	176
5	4·0	4·4	4·3	149	9	0·0	1·9	2·0	52
6	4·5	4·8	5·0	263	10	10·1	10·4	10·4	337
7	4·2	3·3	3·4	299	11	8·4	8·8	8·8	170
8	0·0	1·3	1·3	210	12	7·3	6·7	6·7	322
9	5·0	7·0	7·0	351	13	4·3	5·0	5·0	198

	$\lvert F_o \rvert$	$\lvert F \rvert$	$\lvert F_H \rvert$	$\lvert \alpha^0 \rvert$		$\lvert F_o \rvert$	$\lvert F \rvert$	$\lvert F_H \rvert$	$\lvert \alpha^0 \rvert$
		Calculated					Calculated		
*h*60					*h*80				
0	18·9	20·9	19·3	169	2	6·7	5·7	5·4	278
1	14·0	15·0	14·5	202	3	9·0	8·0	8·0	313
2	10·0	10·7	10·0	231	4	5·7	6·4	6·3	141
3	11·1	10·8	10·4	243	5	5·5	5·4	5·4	343
4	8·1	6·4	7·0	292	6	6·0	8·0	7·8	221
5	5·8	5·0	5·0	136	7	3·0	3·3	2·9	38
6	6·8	6·1	6·5	7	8	0·0	4·3	4·2	177
7	8·1	11·2	9·6	219	9	4·2	4·4	4·7	175
8	4·0	4·0	4·0	18					
9	3·7	4·4	4·3	105	*h*10,0				
10	3·2	3·0	2·9	196					
11	3·5	4·0	3·5	329	0	12·9	13·4	13·5	162
12	5·0	6·0	6·0	204	1	6·1	7·8	8·3	74
					2	0·0	2·6	2·6	148
*h*80					3	0·0	1·6	1·4	225
					4	4·2	3·8	3·7	346
0	8·2	10·0	10·0	27	5	3·7	4·0	3·9	166
1	10·6	10·0	9·9	138	6	4·5	4·2	4·2	339

* These reflexions have been corrected for extinction effects.

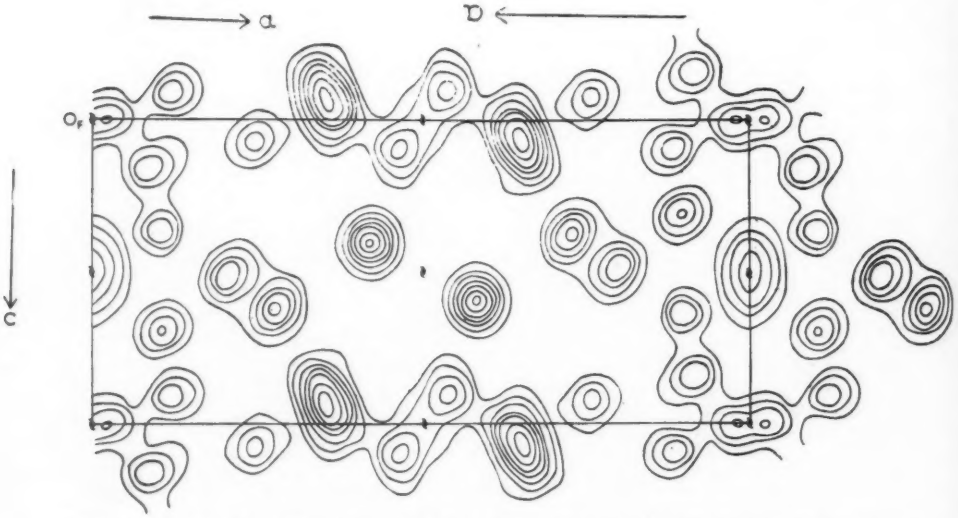

FIG. 7. The final *b*-axis Fourier projection of L-tyrosine hydrochloride. Contours are at intervals of 1·0 *e*/A² starting from 1·0 *e*/A². For chlorine the interval is 2·0 *e*/A².

TABLE VIII

L-tyrosine hydrochloride : Standard deviation in various parameters

Atom	(A)			
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Average
C ..	0·022	0·023	0·023	0·023
N ..	0·018	0·018	0·016	0·017
O ..	0·014	0·016	0·015	0·015
Cl ..	0·0055	..	0·0065	0·0060

Bond (l)	$\sigma(l)$
C—C ..	0·033 (A)
C—N ..	0·029
C—O ..	0·027
O—O ..	0·021

σ in a typical angle in the benzene ring = 2·3°. $\sigma(\rho) = 0{\cdot}2\ e/\text{A}^3$.

DISCUSSION OF THE STRUCTURE

Intra-molecular features.—The interatomic distances and bond angles are listed in Table IX and are shown in Fig. 8. The inter-molecular distances including hydrogen bonds are given in Table X. Figure 9 shows the packing arrangement of the molecules in the unit cell. The notations used in the case of the hydrobromide (Part I) are used in the figures and discussions of the present case also.

Table IX shows that the bond lengths in the benzene ring vary between 1·350 Å and 1·404 Å with an average of 1·385 Å. This average value agrees closely with that (1·39 Å) found in a recent accurate determination of the structure of benzoic acid (Sim, Robertson and Goodwin, 1955). However, the range as well as the average of these bonds are smaller than those of the hydrobromide. The fact that the bonds are rather small on the average is most probably due to the following reason. It might have been noticed that during the refinement of the present compound the hydrogen contribu-

TABLE IX

Inter-atomic distances and bond angles in L-tyrosine hydrochloride

Bond	(*l*)	Atoms	Angle
C_1C_2	1·350 (A)	$C_1—C_2—C_3$	120° 6′
$C_2—C_3$	1·372	$C_2—C_3—C_4$	121° 26′
$C_3—C_4$	1·395	$C_3—C_4—C_5$	117° 42′
$C_4—C_5$	1·399	$C_4—C_5—C_6$	120° 0′
$C_5—C_6$	1·404	$C_5—C_6—C_1$	118° 12′
$C_6—C_1$	1·399	$C_6—C_1—C_2$	120° 42′
$C_4—C_7$	1·522	$O_1—C_1—C_2$	123° 24′
$C_7—C_8$	1·530	$O_1—C_1—C_6$	116° 12′
$C_8—C_9$	1·510	$C_3—C_4—C_7$	119° 12′
$C_1—O_1$	1·374	$C_5—C_4—C_7$	122° 24′
$C_9—O_2$	1·270	$C_4—C_7—C_8$	112° 45′
$C_9—O_3$	1·265	$C_7—C_8—C_9$	110° 6′
$C_8—N$	1·484	$C_7—C_8—N$	110° 48′
		$N—C_8—C_9$	108° 27′
		$C_8—C_9—O_2$	122° 0′
		$C_8—C_9—O_3$	117° 36′
		$O_2—C_9—O_3$	120° 80′

tions were included in the calculation of structure factors at quite an early stage of refinement (when R value was about 20 per cent.). Since these structure factors were used in the refinements they should lead to the correct coordinates which otherwise would have been effectively displaced towards the hydrogens, if the hydrogen contributions had not been included in the structure factors. In other words, the systematic refinement after including the hydrogen contributions seems to be the reason for an effective smaller average value of the bonds and conversely if cycles of refinement are not carried out after the inclusion of hydrogens (as was the case with the hydrobromide) the whole benzene ring would appear slightly larger. This fact seems to have been ignored in most structure determinations resulting in a rather larger value for the average bond in the benzene ring.

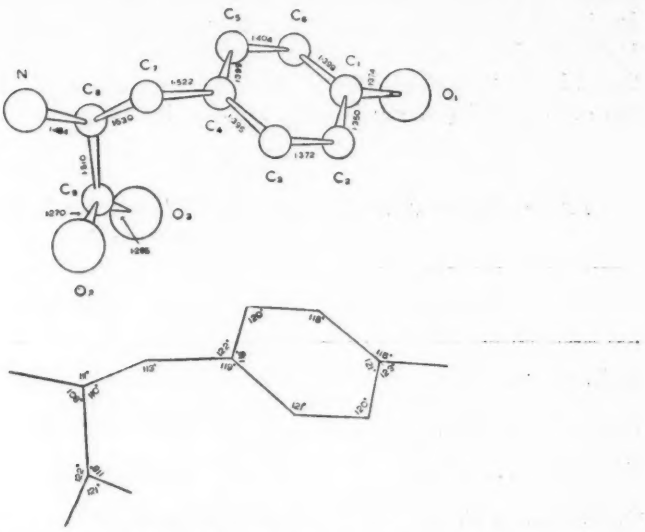

FIG. 8. Observed values of (*a*) bond lengths (in A) and (*b*) bond angles in L-tyrosine hydrochloride.

The equation to the plane of the benzene ring was determined by the method of least squares, and is given by

$$z + 1{\cdot}143\,y - 0{\cdot}570\,x = 1{\cdot}587.$$

The largest deviation of 0·007 Å from this plane occurs for the atom C_4 and the mean deviation (r.m.s.) is only 0·0045 Å. The deviations of the various atoms from this plane are,

$$C_1 = -0{\cdot}0049 \qquad C_2 = 0{\cdot}0056 \qquad C_3 = 0{\cdot}006$$
$$C_4 = -0{\cdot}0068 \qquad C_5 = 0{\cdot}0006 \text{ and } C_6 = 0{\cdot}0043 \text{ Å}$$

This establishes the almost perfect-planarity of the benzene ring. The atoms O_1 and C_7 also lie almost in the same plane, their deviations being respectively + 0·08 and − 0·075 Å. The angles in the benzene ring are also quite normal with an average of 119° 40′.

The bond C_1—O_1 has a length of 1·374 Å and is in good agreement with the values usually reported for a single bond between an aromatic carbon and an oxygen. Examples of such values are 1·36 Å and 1·37 Å in β-resorcinol (Robertson and Ubbelohde, 1938), 1·36 Å in α-resorcinol (Robertson, 1936), 1·38 Å in glycyl-L-tyrosine hydrochloride (Smits and Wiebenga, 1953)

and 1·36 Å in some additional complexes of quinol (Palin and Powell, 1947). In view of the general agreement in the features of the hydrobromide and the hydrochloride, it can be said safely that the rather large value of 1·42 Å found in the former compound (Part I) for the above bond is not real, since the corresponding value is only 1·374 Å in the present case.

TABLE X

Inter-molecular distances, including hydrogen bonds and bond angles in L-tyrosine hydrochloride

Hydrogen bonds		Hydrogen bond angles	
N (M′) H .... Cl′	.. 3·32 (A)	C_8—N (M′)—Cl_{001}	137°
N (M′) H .... Cl'_{001}	3·31	C_8—N (M′)—Cl′	86°
N (M′) H .... O_2 (M_{101})	2·79	C_8—N (M′)—O_2 (M_{101})	124°
O_3 (M′) H .... O_1 (M)	2·50	C_9—O_3 (M′)—O_1 (M)	111°
O_1 (M) H Cl	3·11	C_1—O_1 (M)—Cl	120°

Short Contacts

Cl—C_9 (M_{100})	3·14 (A)
N (M′) —Cl_{001}	3·39
Cl—O_2 (M_{100})	3·42
Cl—O_3 (M_{100})	3·45
C_9 (M)—C_3 (M)	3·62
C_3 (M)—O_3 (M)	3·51

All the C—C distances are close to the standard value. The angles at the aliphatic carbons are also in agreement with the tetrahedral angle of 109° 28′.

The features of the carboxyl group are quite similar to those found in the hydrobromide (Part I). The C_9—O_2 and C_9—O_3 distances are 1·270 and 1·265 Å respectively and are in agreement with the values usually found. The slightly larger values for them as compared with the pure C=O distance (1·215, Pauling, 1945) are also compatible with the finding (*see* discussion

later) that both the oxygens are involved in hydrogen bond formation. The angle 121° for $O_2-C_9-O_3$ may seem to be rather small, at first sight. Now the standard error in bond angles is about 2°. Also, since two of the atoms

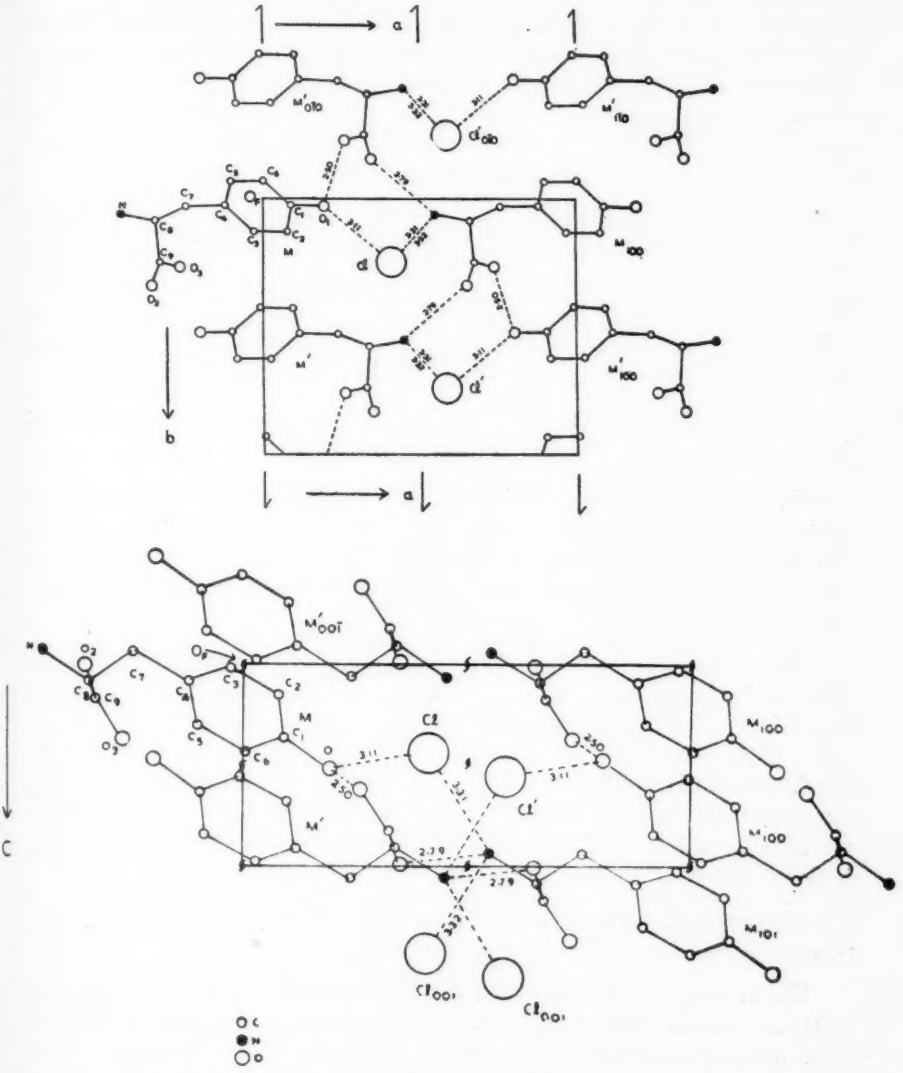

FIG 9. Unit cell of L-tyrosine hydrochloride projected down (*a*) the *c*-axis and (*b*) the *b*-axis. Hydrogen bonds are shown by dotted lines.

C_9 and O_2 are involved in overlap in one projection, the error in the angle can be taken to be slightly larger than 2° and the above deviation of about 4° from the standard expected value of about 125° (Pauling, 1945) is not significant. Moreover, values of 122° in norleucine (Mathieson, 1953), 121° in DL-α-methionine (Mathieson, 1952), 122° in DL-β-methionine (Mathieson, 1952) and 122° in glycyl-L-tryptophan dihydrate (Pasternak, 1956) have also been reported, which are all distinctly less than 125°.

The equation to the plane of the carboxyl group is given by

$$z + 0{\cdot}020\,y - 2{\cdot}049\,x = 8{\cdot}269.$$

The largest deviation from this plane is for the atom O_3 (0·032 Å) and the r.m.s. deviation is 0·017 Å. The deviations of the various atoms are $C_8 = -0{\cdot}004$ Å, $C_9 = 0{\cdot}032$ Å, $O_2 = -0{\cdot}001$ Å and $O_3 = -0{\cdot}017$ Å. The nitrogen is out of this plane by 0·71 Å. As the value seems to vary within wide limits in the various amino acids investigated so far, the value of 0·71 Å in our case does not seem to require any special attention.

The $\alpha C-NH_3^+$ distance is 1·484 Å and is in agreement with that found in the hydrobromide (Part I) and other compounds.

Molecular arrangement and hydrogen bonds.—As is to be expected, the molecular packing arrangement and the scheme of hydrogen bonds are, in the present case, identical with those found in the hydrobromide (Part I). They are therefore discussed only briefly here excepting where they require some explanation.

The rather short OH .... O bond between the oxygen O_1 (M) of the phenolic hydroxyl group and the oxygen O_3 (M′) of the carboxyl group found in the hydrobromide (Part I) is remarkably confirmed in the present case. The value found now, namely, 2·50 Å, is identical with that found in the hydrobromide. The O_1 (M) H .... Cl bond is of length 3·11 Å and agrees well with that found for the hydrobromide namely 3·23 Å, provided we allow for the difference in the ionic radii of bromine and chlorine, which is 0·1 Å (Pauling, 1945).

The angles C_1-O_1 (M)—Cl (120°) and C_9-O_3 (M′) $-$ O_1 (M) (110°) are in good agreement with the tetrahedral angle.

The hydrogen bonds involving the NH_3^+ group are essentially the same as in the previous compound. The slight difficulty experienced in the case of the hydrobromide (Part I) in deciding between NH .... O and NH .... Br bonds practically vanishes here. This is due to the fact that

$N(M')-O_2(M_{101})$ distance is 2·79 Å and considerably shorter than 3·01 Å found in the hydrobromide. This only confirms our previous conclusion that the $N(M')H \ldots O_2(M_{101})$ is the real hydrogen bond and $N(M')H \ldots Cl_{001}$ is not. In fact, the present value of 2·79 Å for the NH .... O bond agrees closely with those observed in other compounds. Examples are: 2·79, 2·81 and 2·87 Å in DL-serine (Shoemaker *et al.*, 1950), 2·73, 2·87 and 2·87 Å in norleucine (Mathieson, 1953), 2·80 and 2·77 Å in DL-methionine (Mathieson, 1952) and 2·75–2·89 Å in glycyl L-typtophan dihydrate (Pasternak, 1956). The slightly shorter length of NH .... O bond is also indicative of the bond being quite strong. The N—Cl distances are $N(M')-Cl' = 3{\cdot}32$ Å, $N(M')-Cl_{001}' = 3{\cdot}3$ Å and $N(M')-Cl_{001} = 3{\cdot}39$ Å. The corresponding distances in the hydrobromide are 3·45, 3·45 and 3·50 Å and hence the two compounds closely agree in their relative distances also. The fact that $N(M')-Cl_{001}$ is slightly larger than the other two which are almost equal (3·32 and 3·31 Å) also supports our previous conclusion that the former is not a hydrogen bond. The hydrogen bond angles near the NH_3^+ groups are also quite satisfactory.

There is also a short Van der Waals contact between $C_9(M_{100})$ and Cl. Its value is 3·14 Å. This short contact has also been observed in the hydrobromide (Part I) where it has the value 3·30 Å. The difference between the two is also just the difference in the ionic radii of bromine and chlorine. This short contact is thus established by way of confirmation, in the two compounds. Examples of short contacts have already been cited (Part I). In fact, the short OH .... O bond coupled with the above short C_9—X (X stands for Cl or Br) contact seems to be an important feature in the two structures. It shows how, under conditions peculiar to a particular structure, some of the bonded and non-bonded distances can vary over fairly wide limits, while, of course, most of the other bonds are normal.

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INFRA-RED SPECTRA OF FLUOROXYLENES

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Abstract

The infra-red spectra of four fluoroxylenes (1, 2, 6-, 1, 2, 3-, 1, 3, 4- and 1, 2, 5-isomers) have been recorded in the 2–15 μ region on a Perkin-Elmer Model 21 spectrophotometer. From among the bands recorded, those which could be correlated to the fundamental vibration of the constituent benzene and methyl groups are discussed in detail and compared with particular reference to the type of substitutions.

Several methyl benzenes were studied wit refehrence to their vibration spectra by Pitzer and Scott.[1] Among them were the xylenes whose vibration frequencies he assigned and correlated to benzene and methyl vibrations. Recently Wilmshurst and Bernstein[2] have studied toluene and *m*-xylene, in the light of fresh frequency assignments by Ingold *et al.*[3] and Mair and Hornig.[4]

The infra-red spectra of several fluorinated benzenes have been studied by Nielsen *et al.*[5, 6] The main approach of these workers has been the classification of the frequencies into the different symmetry species. Several workers have studied the vibrations belonging to the methyl group in particular. Among them may be mentioned Fox and Martin[7] and Sheppard and Simpson.[8] The latter workers classify the methyl vibrations as the internal and external vibrations. Randle and Whiffen[9] have studied a number of compounds with particular reference to the CH_3 rocking modes. Barcelo and Bellanato[10] in their study of methyl amines make a comparison of the relative intensities in the Raman and Infra-red spectra of the internal C–H stretching and bending vibrations of the methyl group.

It is proposed to study in the present investigation, the infra-red spectra of four isomeric fluoroxylenes. They may be called 1, 2, 6-, 1, 2, 3-, 1, 3, 4- and 1, 2, 5-fluoroxylenes and are represented diagrammatically on next page.

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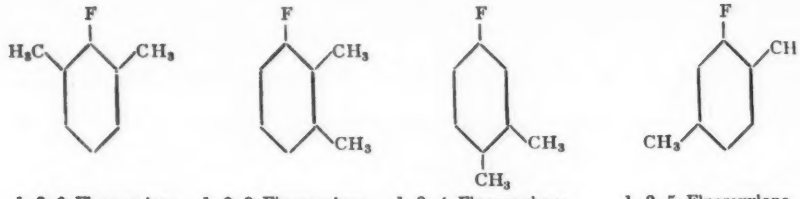

1, 2, 6-Fluoroxylene (I) 1, 2, 3-Fluoroxylene (II) 1, 3, 4-Fluoroxylene (III) 1, 2, 5-Fluoroxylene (IV)

EXPERIMENTAL

The compounds were prepared in this laboratory from the corresponding xylidines and were found to be pure. The infra-red spectra were recorded on the Perkin-Elmer Model 21 double beam instrument with linear wavelength scale, principally using the sodium chloride prism. The C–H stretching frequency region was recorded also with the lithium fluoride prism. The spectra were recorded using the liquid as such with a compensating sodium chloride window in the other beam. Cell thicknesses of 0·1 mm. and 0·025 mm. were used. In the case of very strong bands the substance was taken as a thin film in between two sodium chloride windows. The infra-red spectra in the sodium chloride region are reproduced in Fig. 1.

RESULTS AND DISCUSSION

Among the four compounds under consideration, compound I belongs to the C_{2v} group and the rest to C_s. Out of the 48 fundamental vibrations for each molecule, 30 will belong to the phenyl part and 18 to the CH_3 part. For the C_{2v} group the 48 vibrations get divided into the respective species as $16\,a_1 + 7\,a_2 + 10\,b_1 + 10\,b_2$. Here the x-axis is taken perpendicular to the plane of the molecule and the z-axis is taken as the two-fold axis as suggested by the Joint Commission on spectroscopy. All are allowed in the Raman effect and all but the a_2 vibrations in the infra-red. For the C_s group the species division will be $31\,a' + 17\,a''$.

The main interest in the present study of these spectra is to view them in the context of the analyses of the spectra of xylenes by Pitzer and Scott[1] and *m*-xylene by Wilmshurst and Bernstein.[2] The latter's assignments are consistent with vapour band contours, depolarisation ratios, the Teller-Redlich product rule and a modified form of this rule suggested by Pitzer and Scott. Also of interest will be the effect of fluorine substitution on the phenyl and methyl vibration frequencies. Now it is proposed to analyse separately the phenyl and methyl vibrations. In Table I are presented the frequencies recorded for the four compounds along with their intensities.

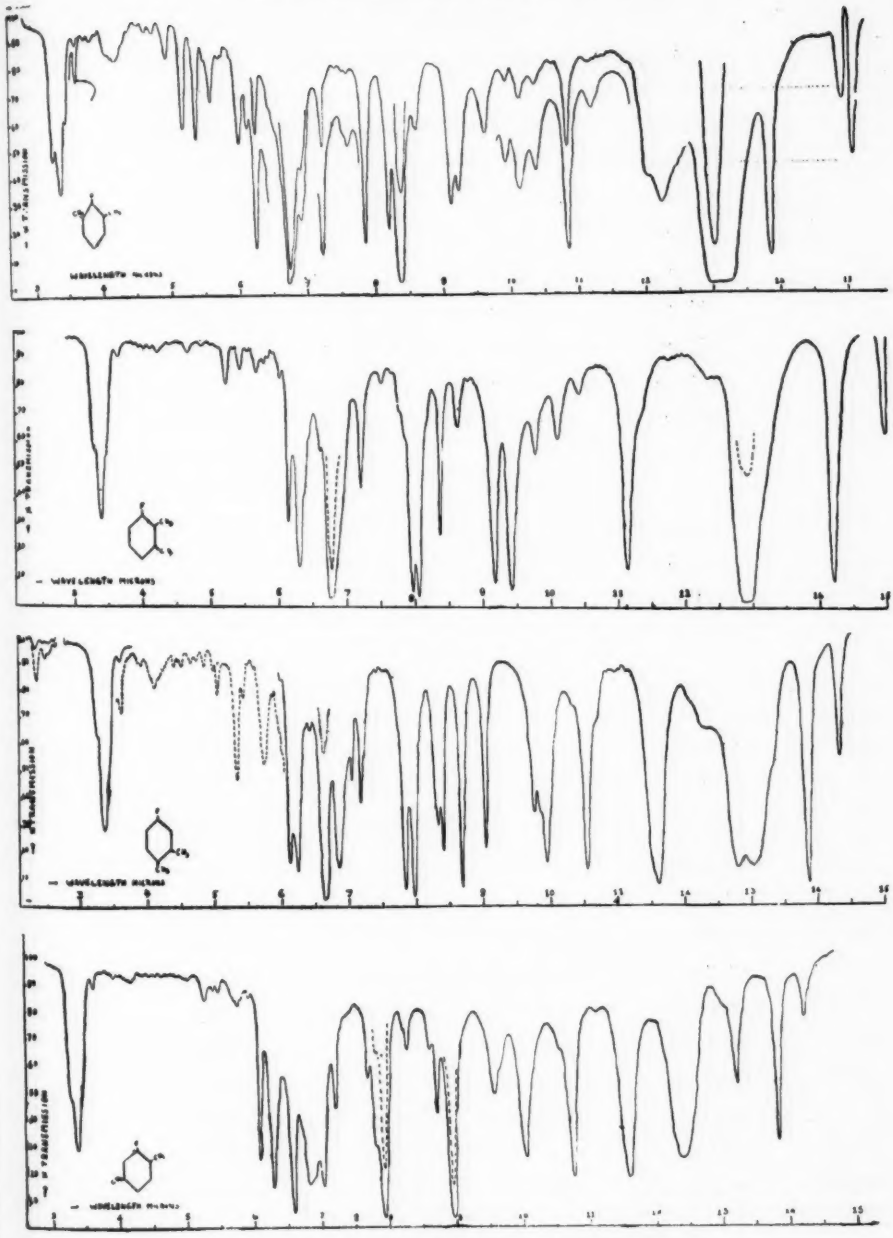

FIG. 1. Infra-red Spectra of Fluoroxylenes.

TABLE I

Infra-red frequencies of fluoroxylenes ($cm.^{-1}$)

Compound I	Compound II	Compound III	Compound IV
662 *m*	667 *w*	696 *m*	701 *vw*
721 *s*	703 *s*	720 *s*	721 *s*
768 *s*	773 *s*	749 *m*	756 *m*
817 *s*	776 *s*	765 *s*	806 *s*
828 *m*	884 *w*	781 *s*	861 *s*
891 *vw*	898 *s*	860 *s*	928 *s*
920 *m*	959 *w*	931 *w*	946 *vw*
963 *w*	989 *w*	947 *s*	995 *s*
987 *w*	1022 *m*	1004 *s*	1043 *m*
1006 *w*	1062 *s*	1012 *s*	1116 *s*
1038 *m*	1089 *s*	1024 *s*	1144 *m*
1081 *s*	1159 *w*	1105 *s*	1157 *w*
1095 *s*	1195 *s*	1151 *s*	1205 *w*
1157 *m*	1224 *w*	1188 *s*	1215 *w*
1193 *s*	1241 *s*	1199 *s*	1259 *s*
1220 *s*	1255 *s*	1253 *s*	1279 *w*
1272 *s*	1258 *s*	1276 *s*	1297 *w*
1312 *w*	1274 *w*	1391 *m*	1383 *m*
1383 *m*	1285 *w*	1416 *m*	1420 *s*
1445 *s*	1332 *vw*	1460 *s*	1447 *s*
1475 *s*	1389 *s*	1499 *s*	1453 *s*
1484 *s*	1458 *s*	1506 *s*	1462 *s*
1600 *m*	1477 *s*	1603 *s*	1517 *s*
1629 *vw*	1513 *m*	1631 *s*	1589 *s*
1650 *vw*	1550 *m*	1658 *w*	1642 *s*
1658 *w*	1570 *s*	1698 *vw*	1684 *w*
1686 *vw*	1587 *s*	1731 *w*	1722 *w*
1736 *vw*	1631 *s*	1821 *vw*	1725 *w*

TABLE I—*Contd.*

Compound I	Compound II	Compound III	Compound IV
1777 *vw*	1655 *vw*	1865 *w*	1737 *w*
1808 *vw*	1695 *vw*	1968 *vw*	1743 *w*
1850 *w*	1712 *vw*	1995 *vw*	1808 *w*
1923 *w*	1730 *vw*	2049 *vw*	1811 *w*
1997 *vw*	1759 *vw*	2094 *vw*	1834 *w*
2009 *vw*	1793 *vw*	2129 *vw*	1884 *w*
2042 *vw*	1836 *vw*	2195 *vw*	1976 *vw*
2091 *vw*	1877 *vw*	2221 *vw*	1997 *vw*
2141 *vw*	1912 *w*	2249 *vw*	2011 *vw*
2188 *vw*	1915 *w*	2395 *vw*	2040 *vw*
2257 *vw*	1958 *vw*	2415 *vw*	2070 *vw*
2296 *vw*	1997 *vw*	2438 *vw*	2100 *vw*
2325 *vw*	2053 *vw*	2518 *vw*	2136 *vw*
2352 *vw*	2138 *vw*	2556 *vw*	2185 *vw*
2380 *vw*	2150 *vw*	2631 *vw*	2232 *vw*
2409 *vw*	2192 *vw*	2659 *vw*	2262 *vw*
2432 *vw*	2247 *vw*	2695 *vw*	2298 *vw*
2456 *vw*	2282 *vw*	2735 *w*	2344 *vw*
2518 *vw*	2311 *vw*	2762 *vw*	2363 *vw*
2541 *vw*	2432 *vw*	2869 *m*	2409 *vw*
2567 *vw*	2478 *vw*	2923 *s*	2435 *vw*
2597 *vw*	2531 *vw*	2945 *s*	2468 *vw*
2645 *vw*	2567 *vw*	2975 *s*	2525 *vw*
2680 *vw*	2587 *vw*	3029 *m*	2567 *vw*
2739 *w*	2634 *vw*	3058 *w*	2735 *w*
2856 *m*	2735 *w*	3115 *w*	2865 *m*
2923 *s*	2762 *vw*		2927 *s*
2953 *s*	2869 *m*		2949 *s*
2980 *s*	2927 *s*		2971 *m*
3029 *s*	2949 *s*		3025 *m*
3048 *s*	2975 *m*		3053 *w*
3067 *m*	3034 *m*		3086 *w*
	3071 *m*		

The phenyl vibrations.—The proposed fundamental vibrations belonging to the phenyl part, together with their symmetry and the corresponding benzene modes, are given in Table II.

TABLE II

Fundamental vibrations of phenyl part (cm.$^{-1}$)

Mode	Species				Compounds				
	C_s	C_{2v}	D_{6h}		Benzene	I	II	III	IV
ν CC	a'	a_1	a_1g	ν_1	992	768	773	781	806
	a'	b_2	b_2u	ν_{14}	1310	1312	1332	..	1297
	a'	a_1	e_u^-	ν_{19a}	1485	1484	1477	1506	1517
	a'	b_2	e_u^-	ν_{19b}	1485	?	?	?	?
	a'	a_1	e_g^+	ν_{8a}	1596	1629	1631	1631	1642
	a'	b_2	e_g^+	ν_{8b}	1596	1600	1587	1603	1589
β CH	a'	a_1	e_g^+	ν_{9a}	1178	1157	1159	1151	1144
	a'	b_2	e_g^+	ν_{9b}	1178	..	..	..	..
	a'	a_1	e_u^-	ν_{18a}	1033	..	..	..	..
	a'	b_2	e_u^-	ν_{18b}	1033	..	..	..	..
	a'	b_2	b_2u	ν_{15}	1150	1095	1089	1105	1116
	a'	b_2	a_2g	ν_3	1326	?	?	?	?
γ CH	a''	b_1	a_2u	ν_{11}	671	..	..	..	..
	a''	a_2	e_g^-	ν_{10a}	850	..	..	..	..
	a''	b_1	e_g^-	ν_{10b}	850	..	..	..	..
	a''	a_2	e_u^+	ν_{17a}	970	891	884	860	861
	a''	b_1	e_u^+	ν_{17b}	970	920	898		928
	a''	b_1	b_2g	ν_5	985	963	959	947?	946
β CC	a'	a_1	b_1u	ν_{12}	1010	1006	989	1004	995
	a'	a_1	e_g^+	ν_{6a}	606	662?	667?	696?	701?
	a'	b_2	e_g^+	ν_{6b}	606	..	..	..	..
γ CC	a''	b_1	b_2g	ν_4	703	721	703	720	721
	a''	a_2	e_u^+	ν_{16a}	404	..	..	..	..
	a''	b_1	e_u^+	ν_{16b}	404	..	..	..	..
ν C—X		C–CH_3				1193	1195	1199	1205
		C–CH_3				1272	1255	1276	1279
		C–F				1220	1241	1253	1259

Pitzer and Scott have assigned the benzene breathing vibration of 992 cm.$^{-1}$ at about 1000 cm.$^{-1}$ in toluene and *m*-xylene. Wilmshurst and Bernstein have assigned a value between 700–800 cm.$^{-1}$ in the case of *m*-xylene. These latter authors observe that the C–CH_3 stretching vibration and the ring vibration interact bringing down the ring vibration frequencies. In the case of fluoroxylenes the value of about 760 cm.$^{-1}$ for this vibration seems reasonable in view of a recent systematisation by Padhye and Viladkar.[11] It is observed that in compound IV the strong band at 806 cm.$^{-1}$ is assigned to this vibration in preference to a weak one at 756 cm.$^{-1}$ One component of the benzene ν_{19} vibration at 1485 cm.$^{-1}$ should normally be about 1450–1500 cm.$^{-1}$ and the other about 1375–1400 cm.$^{-1}$, in substituted benzenes. This region is crowded because of the presence of the CH_3 internal bending modes. The band in the region 1450–1500 cm.$^{-1}$ gives a broad appearance in I and II whereas it is well separated in III and IV. There seems to be a superposition of three bands in this region. Two of these around 1450 cm.$^{-1}$ belong to the CH_3 asymmetric bending modes and the third one corresponds to one component of the 1485 cm.$^{-1}$ vibration of benzene. The compounds III and IV show additional strong bands at 1416 cm.$^{-1}$ and 1420 cm.$^{-1}$ respectively. These could be an internal methyl bending mode or correspond to the other component of the benzene 1485 cm.$^{-1}$ vibration. From intensity consideration they are tentatively assigned to the CH_3 internal deformation mode.

In the 1600 cm.$^{-1}$ region there are two strong bands corresponding to the benzene 1596 cm.$^{-1}$ vibration. The separation of these bands in xylenes and disubstituted benzenes is low. For trisubstituted benzenes the separation is shown to be rather high.[12] In this respect it is observed that II and IV on the one hand and the other two on the other show some similarity.

The weak bands around 1300 cm.$^{-1}$ have been assigned to correspond to the benzene ν_3, 1310 cm.$^{-1}$ vibration. The compound IV however does not show this band.

Among the C—C bending vibrations, the ν_{12}, 1010 cm.$^{-1}$ vibration of benzene appears at around 1000 cm.$^{-1}$ in these compounds. It is weak or absent in the I and II compounds and strong in the other two. The other C–C bending modes that can be identified are discussed at the end.

To make the assignment of the C–H stretching modes of the phenyl part more convenient, the spectra of xylenes in this region have been recorded with the lithium fluoride optics. They show four bands in this region whereas in fluoroxylenes, there are only three as shown in Table III and it seems that in each case a band near 3010 cm.$^{-1}$ is lost on fluorine substi-

tution. The four fluoroxylenes can be grouped in two types for the analysis of these vibrations; those having substitution at 1, 2, 3 and those at 1, 2, 4. Compound I and II fall into the first type and II and IV compounds fall into the latter. The former have three bands near 3060, 3040 and 3030 cm.$^{-1}$ whereas the latter have them near 3090, 3060 and 3040 cm.$^{-1}$ It thus seems that in addition to the C–H valence vibrations lost in xylenes, in the '1, 2, 3' type of compounds, the other component of ν_{20} 3080 cm.$^{-1}$ frequency is changed to a C–X mode, whereas, in the '1, 2, 4' type of compounds one of ν_7 3047 cm.$^{-1}$ vibration is lost.

TABLE III

Phenyl ν C–H frequencies (cm.$^{-1}$)

o-xylene	*m*-xylene	*p*-xylene	Compounds			
			I	II	III	IV
3100 ..	3096	3096	3067	3071	3115	3086
3053 ..	3044	3049	3048	..	3058	3053
3016, 3016 unresolved	3025, 3012	3021, 3003	3029 ..	3034 ..	3029 ..	3025 ..

The C–H inplane bending modes are expected to occur in the region 1050–1300 cm.$^{-1}$ In the case of fluoroxylenes, we expect only three vibrations. In all the compounds of the present investigation we get a band around 1100 cm.$^{-1}$ which may be assigned to the ν_{15}, 1150 cm.$^{-1}$ vibration of benzene. Again in all the compounds there is a band around 1150 cm.$^{-1}$ This can be correlated with ν_{9a}, 1178 cm.$^{-1}$ vibration in benzene. It may be noted that the band at 1151 cm.$^{-1}$ in compound III is quite strong when compared to the other three compounds. The third frequency belonging to this mode cannot be fixed because of the overlapping by the C–CH_3 and C–F stretching vibrations in the region.

We expect three vibrations belonging to C–H out of plane mode. We get in all the cases one band between 860–890 cm.$^{-1}$ and another between 900–930 cm.$^{-1}$ These may correspond to the two components of ν_{17} 970 cm.$^{-1}$ vibration of benzene. There are weak bands at 963 cm.$^{-1}$, 959 cm.$^{-1}$ and 946 cm.$^{-1}$ in compounds I, II and IV. These may correspond to the ν_5, 985 cm.$^{-1}$ vibration of benzene. There is a strong band at 947 cm.$^{-1}$ in the

III compound. In addition we have bands around 820 cm.$^{-1}$ of medium intensity in compound I.

TABLE IV

CH_3 vibrations (cm.$^{-1}$)

Mode	Compound I	Compound II	Compound III	Compound IV
Asymmetric stretching	2980	2975	2975	2971
	2953	2949	2945	2949
	2923	2927	2923	2927
Symmetric stretching	2856	2869	2869	2865
Asymmetric bending	1475	1458	1460	1453
	1445	..	1416	1420
Symmetric bending	1383	1389	1391	1383
Rocking	1081	1062	1024	1043
	1038	1022	947 ?	..
Torsion	..	..	..	..

Among the C–X vibrations, where X is the substituent—in this case CH_3 and F—the bending ones are all below 600 cm.$^{-1}$ and so fall out of the range covered in the present investigation. The C–F stretching mode has been fixed at 1220, 1241, 1253 and 1259 cm.$^{-1}$ in compounds I, II, III and IV respectively. This is in accord with the values assigned by Nielsen *et al.*[5, 6] for this vibration.

Randle and Whiffen[9] attribute a frequency of 793 cm.$^{-1}$ in hexamethyl benzene to the C–CH_3 stretching mode. On the other hand Hastings and Nicholson[13] have calculated this frequency to be 1385 cm.$^{-1}$ In toluene, Pitzer and Scott[1] as well as Wilmshurst and Bernstein[2] assign a frequency around 1210 cm.$^{-1}$ to this mode. Again the latter workers assign 1170 cm.$^{-1}$ and 1248 cm.$^{-1}$ to these modes in *m*-xylene. Consistent with these observations, it is proposed in the present series of compounds to assign one frequency around 1190 cm.$^{-1}$ and another around 1270 cm.$^{-1}$ to these modes. The C–X stretching modes have also been included in Table I.

CH_3 internal vibrations.—The assignment of fundamentals belonging to the CH_3 groups are shown in Table IV. There must be six stretching frequencies, two of symmetric and four of asymmetric type. Whereas Pitzer and Scott have kept all the frequencies coincident at 2950 cm.$^{-1}$, Wilmshurst and Bernstein account for these with two vibrations at 2923 and 2953 cm.$^{-1}$ In the present investigation four vibrations have been recorded in this region with the help of lithium fluoride optics, in all the cases. The vibration at about 2860 cm.$^{-1}$ may be taken as the symmetric stretching and the vibrations above 2900 cm.$^{-1}$ may be taken as the asymmetric stretching.

The band at 2860 cm.$^{-1}$ corresponding to a polarised Raman line in *m*-xylene has been assigned as an overtone by Wilmshurst and Bernstein, and they have assigned the band at 2923 cm.$^{-1}$ to symmetric C–H stretching of the methyl group. The 2923 cm.$^{-1}$ band is polarised in the Raman spectrum. Several earlier workers, on the other hand, have assigned a frequency around 2860 cm.$^{-1}$ to the symmetric C–H stretching of the CH_3 group and the bands above 2900 cm.$^{-1}$ to asymmetric C–H stretching in a methyl substituted aromatic compound.

The polarisation data in such cases is however tentative. Apart from the fact that there is a large amount of overlapping of the bands, the symmetry assignment of the internal modes of substituent groups have to be considered from the over-all symmetry point of view. This is specially important in non-planar substituents. In the present case one of the asymmetric C–H stretching vibrations of the methyl group under reduced symmetry would reduce to a totally symmetric vibration. Hence the vibrations around 2920 cm.$^{-1}$ have been assigned to the asymmetric C–H stretching vibration of the CH_3 group.

As for the bending modes we get in all cases a band around 1385 cm.$^{-1}$ which can be attributed to the symmetric bending mode. Again the bands around 1450 cm.$^{-1}$ in all the compounds have been assigned to the unsymmetrical bending mode. We get two bands each in the I, III and IV compounds, corresponding to this mode.

The bands at 1038 cm.$^{-1}$ and 1081 cm.$^{-1}$ in I are assigned to the rocking mode in line with similar assignment by Wilmshurst and Bernstein in *m*-xylene. The bands at 1022 and 1062 cm.$^{-1}$ in the II compound and at 1,043 cm.$^{-1}$ in the IV compound have also been assigned to this mode. In the case of compound III there is a band at 1024 cm.$^{-1}$ and another strong band at 947 cm.$^{-1}$ It is to be considered whether both of these can be the rocking modes, as per Randle and Whiffen's contension. According to these workers, for compounds with two adjacent methyl groups without

any other group adjacent to them, one should expect two bands at 995 cm.$^{-1}$ and 1022 cm.$^{-1}$ corresponding to the rocking modes. There are in the case of III, three bands at 947, 1004 and 1024 cm.$^{-1}$ It is likely that the methyl rocking vibration and the vibration around 1000 cm.$^{-1}$ interact to give the anomalous intensity pattern for bands at 947 and 1004 cm.$^{-1}$ in this compound.

In the case of IV, the intensity distribution of the bands suggests a similar interaction.

A few more observations can be made about the spectra of these compounds. They arise out of the consideration that the fluoroxylenes can be compared to the corresponding trimethyl benzenes taking into account the fact that the masses of fluorine and a methyl group are nearly the same as has been done by Ferguson *et al.*[14] in the case of fluorotoluene. The 1, 2, 3-trimethyl benzene has two strong bands in the region 650–900 cm.$^{-1}$ at 709 and 766 cm.$^{-1}$ The 1, 2, 4- trimethyl benzene, on the other hand, has three strong bands in the same region at 703, 806 and 873 cm.$^{-1}$ The compounds I and II which correspond to 1, 2, 3-trimethyl benzene have strong bands near 660, 720 and 770 cm.$^{-1}$ The compounds III and IV which correspond to 1, 2, 4-trimethyl benzene have bands near 700, 720, 760 800 and 860 cm.$^{-1}$ The two bands near 760 and 800 cm.$^{-1}$ possibly show that the bands at 768 and 773 cm.$^{-1}$ in compounds I and II respectively may be the superposition of two bands which are only resolved in the '1, 2, 4' type of compounds. The higher frequency is assigned to the ring breathing vibration and the lower one probably is a γ-C–H vibration. Compounds III and IV show an additional strong band at near 860 cm.$^{-1}$ characteristic of this type of substitution. This is corroborated by the band at 878 cm.$^{-1}$ in 1, 2, 4-trimethyl benzene.

Both types of trimethyl benzenes show only one strong band around 700 cm.$^{-1}$ Among the xylenes only *m*-xylene shows a strong band in this region. In fluoroxylenes there are two bands in the region. One near 660 cm.$^{-1}$ in 1, 2, 3 type of compounds or near 700 cm.$^{-1}$ in 1, 2, 4 type of compounds and the other near 720 cm.$^{-1}$ in all the four compounds. It is likely that the band near 720 cm.$^{-1}$ may correspond to the band near 700 cm.$^{-1}$ in the 1, 2, 3- and 1, 2, 4-trimethyl benzenes and which from the comparison of xylenes arises due to meta-substitution. The 660–700 cm.$^{-1}$ band may be due to fluorine substitution or one of the components of the benzene 606 cm.$^{-1}$ vibration which has been displaced to this region.

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Q-MULTIPLICATION FOR INCREASING NUCLEAR MAGNETIC RESONANCE SIGNALS*

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1. Introduction

In a nuclear magnetic resonance experiment, when the coil containing the sample is resonated by a capacitor and the circuit fed from a constant current source, the voltage drop across the coil is given by the approximate relation

$$v \simeq v_0 [1 - i 4\pi Q f \chi],$$

assuming $|4\pi Q f \chi| \ll 1$. Here v_0 is the voltage far off nuclear resonance, Q is the quality factor of the circuit, χ is the complex r.f. nuclear susceptibility and f is the filling factor representing the fraction of the coil's magnetic energy stored in the sample. We note that both the absorption and dispersion components of the nuclear magnetic resonance signal are proportional to the Q of the circuit.

Due to skin-effect, the dielectric losses in the coil form and the presence of a metallic shield round the coil, the values of Q attained by experimenters in this field have rarely exceeded 250, a common value being about 100.

While improvements in the mechanical and electrical design of the coil are not likely to be of much help, it is possible to increase considerably the effective Q of the circuit by the use of an active network to supply energy to the tuned circuit to compensate for its losses. This can be achieved by introducing a shunt negative resistance in parallel with the coil.

2. Principle of Q-Multiplication

If we assume that the shunt resistance of the tuned circuit at resonance is R and that a negative resistance $-R_n$ is introduced in parallel with it, the effective shunt resistance becomes

$$\frac{RR_n}{R_n - R}.$$

* Based on a paper read at the Low Energy Nuclear Physics Symposium, held at Bombay, on 27-28th February, 1958, under the auspices of the Department of Atomic Energy.

This corresponds to a multiplication of the original Q of the circuit by the ratio

$$q \equiv \frac{Q_{eff}}{Q_0} = \frac{R_n}{R_n - R}.$$

The Q-multiplication can in principle be made arbitrarily large by letting R_n approach R. If positive feedback is introduced through the resistor R_f from an amplifier of gain A and internal resistance R_i (*see* Fig. 1), it can be

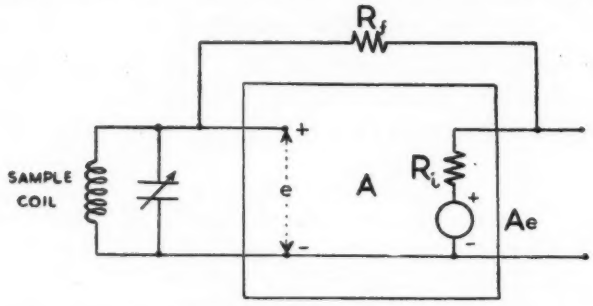

FIG. 1. Basic circuit of the Q-multiplier using shunt negative resistance.

easily shown that

$$-R_n = -\frac{R_f}{A-1} - \frac{R_i}{A-1},$$

assuming the input impedance of the amplifier to be large compared to the other circuit resistances. As the circuit will break into oscillations when R_n becomes equal to R, the gain of the amplifier has to be stabilised by a high degree of negative feedback (Ginzton, 1945) and a high stability resistor has to be used for R_f.

3. NUCLEAR MAGNETIC RESONANCE EXPERIMENTS WITH A Q-MULTIPLIER

Experiments on proton resonance in a sample of water, treated with ferric nitrate solution, were conducted with the amplitude bridge (Thomas and Huntoon, 1949). A Q-multiplier of the type described by Harris (1951), which employs a single tube acting as a cathode follower in the feedback path, and consequently has a high inherent stability, was used. A minor modification to the Q-multiplier involved the application of feedback to the junction between two fixed capacitors connected in series across the main tuning condenser instead of splitting the latter. The complete circuit is given in Fig. 2. A brief analysis of the circuit, neglecting stray capacitances,

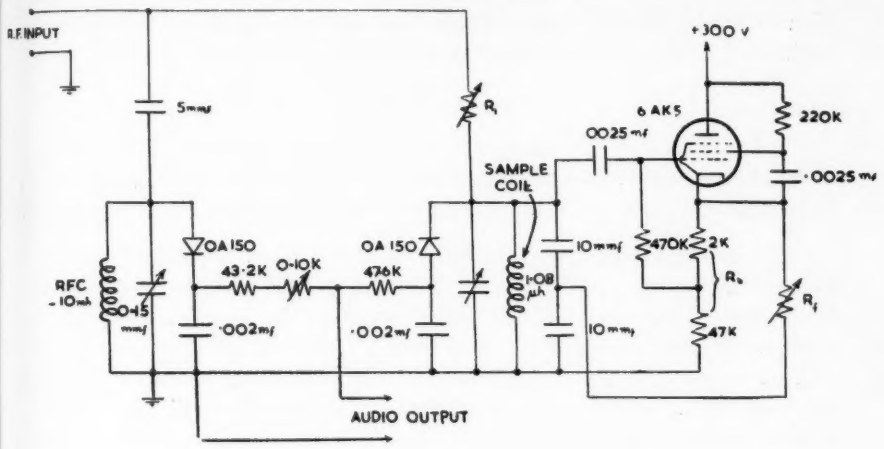

FIG. 2. Amplitude bridge with a Q-multiplier.

shows that the effective negative shunt resistance introduced across the coil is

$$-R_n = -4 \cdot \frac{R_k r_p + R_f \{(\mu + 1) R_k + r_p\}}{(\mu - 1) R_k - r_p},$$

where r_p and μ are respectively the plate resistance and amplification factor of the tube.

The variable resistance R_1 served to maintain a given voltage across the coil for different effective values of Q. At a frequency of 7·35 Mc./S., a maximum increase in signal strength by a factor of about 5 was observed. The Q-multiplication achieved was limited because the shunt resistance of the tuned circuit (about 3,500 Ohms) was smaller than the magnitude of the minimum shunt negative resistance that could be generated by this simple Q-multiplier. It is, however, ideally suited for work in low field NMR spectroscopy, for the shunt resistance of the tuned circuit encountered there is quite high, a typical value being 780 KΩ at 50 Kc./s. (Brown, 1950). At frequencies of the order of a few megacycles, it is desirable to use an amplifier with a stabilised gain of about 10.

Another design criterion that has to be borne in mind at high frequencies is to satisfy the condition that the circuit be fed from a constant current source even at high values of the Q-multiplication factor for maximum benefit. A 0·1 mmf. capacity between the r.f. input point and the terminal of the tuned circuit at 20 Mc./s. corresponds to a reactance of about 80 KΩ whereas the effective shunt resistance of the tuned circuit at a Q_{eff} of 5,000 may be

of the order of 200 KΩ. This difficulty does not arise in the nuclear induction method of resonance detection (Suryan, 1958).

4. DISCUSSION

Q-multiplication can enable effective Q's of the order of 10,000 or more to be achieved without undue difficulty. This will lead to a hundred-fold or even greater increase in the strength of nuclear magnetic resonance signals.

If q is the Q-multiplication ratio, it may appear from the formula of Bloembergen *et al.* (1948) that, for a detecting system whose band width is determined by the final phase-sensitive detector, the signal-to-noise voltage ratio should also increase by a factor $\sqrt{q}$. This is, however, not so because both the nuclear magnetic resonance voltage and the thermal noise voltage generated in the sample coil are affected equally by the feedback. But the amplifier noise at the output will be somewhat less due to the lower amplification now required. There might also be a slight improvement for an oscillographic display due to the increased selectivity of the circuit.

Recently Benoit, Grivet and Guibé (1958) have independently appreciated the advantage of increasing Q by positive feedback in the design of a maser based purely on nuclear magnetic resonance.

5. SUMMARY

A method of increasing the strength of nuclear magnetic resonance signals by factors up to 100 or even more is suggested. The principle is to increase the quality factor Q of the coil containing the sample by means of positive feedback. Experiments on proton resonance in water, treated with ferric nitrate solution, using a Q-multiplier with the amplitude bridge, are described.

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ON THE SYNTHESIS OF FINITE SEQUENTIAL MACHINES*

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Abstract

Starting from the studies of Kleene and Mealy on sequential machines, in this paper is presented a formalism which, in a sense, unifies their treatments. From the specification of the required machine behaviour in terms of events and associated output states, a uniform procedure is given for obtaining a transition table and from that a minimal machine, whenever such a complete reduction is possible. The various steps of the synthesis procedure are so stated that they can be easily programmed on a computer.

1. Introduction

In recent years, sequential machines have been extensively studied under the guise of nerve nets,[1] switching networks[2, 3, 4] and automata.[5] For the present purpose, we take as our point of departure the presentations of Kleene[1] and Mealy[4] and make free use of the concepts introduced by them wherever convenient. In several respects these two papers complement each other and, together, go a long way towards the solution of the synthesis problem, as we shall presently explain.

A sequential machine is described in terms of a finite set of input states, a finite set of output states and a finite set of internal states. It is assumed that the *present output state* (O_t) and the next *internal state* (S_{t+1}) are uniquely determined by the *present internal state* (S_t) and the *present input state* (I_t). Here, t is the time parameter and it is understood that the machine is synchronous, in that, changes in the states take place at discrete instants of time t_i ($i = 1, 2, 3, \ldots$).

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* Since we shall be concerned only with finite sequential machines in this paper, we shall henceforth drop the attribute 'finite'.

When the first draft of this was ready, we received a copy of the paper "Analysis of Sequential Machines—I" by D. D. Aufenkamp and F. E. Hohn. Aufenkamp and Hohn are also concerned with the development of a formalism in terms of which the analysis of a sequential machine can be readily mechanised. However, their approach is entirely different from ours. We are grateful to Professor Hohn for making a copy of the paper available to us.

The problem of analysis of a given sequential machine is one of a *complete* description of its behaviour. This can be done by either of two equivalent methods:

(1) The first method makes use of a Transition table or a state diagram which specifies exhaustively for each pair of present internal—present input states, what the associated pair of next internal—present output states is. This is the approach taken by Mealy.

(2) The second method makes use of the notion of events. Events are input state sequences of finite length. For definiteness, assume that the sequential machine starts with a distinguished internal state. Then its complete behaviour is described by giving its output for each possible event. This is the method followed by Kleene. In his paper, he has answered *in principle* the basic question, what classes of events are representable by sequential machines? The formalism, developed with this in view, allows him to suggest a solution to the synthesis problem, *viz.*, how to construct a sequential machine to represent a given event? However, his solution to this is mostly of academic interest.

Neither of these two methods by itself seems to be adequate enough to answer satisfactorily the synthesis problem. In the synthesis of sequential machines one has three major aspects to contend with, *viz.*,

(*a*) specification of the required behaviour,

(*b*) translation of the specification to a state diagram and the reduction of equivalent internal states, and

(*c*) translation of the reduced state diagram to hardware.

Mealy, in extending the works of Huffman and Moore, confines his consideration almost exclusively to aspects (*b*) and (*c*), *i.e.*, given a transition table or, equivalently, a state diagram, he develops procedures to reduce it to its minimal form and to realise it in terms of circuitry. Kleene, on the other hand, is concerned primarily with aspect (*a*) of the problem, *i.e.*, the development of adequate concepts to describe (and hence, equivalently, to specify) the machine behaviour in terms of its input states and output states.

Thus, it would seem natural to look for a unified treatment which would exploit equally methods 1 and 2 described earlier and, hence, treat adequately all the 3 aspects of the synthesis problem. Clearly, a prerequisite for such a unification is the availability of a simple procedure which will enable one to go from a description of machine behaviour by method 2 to a description of its behaviour by method 1.

In this paper we present a formalism which enables one to proceed from a specification of the required machine behaviour in terms of events and associated outputs to a transition table. From this initial transition table a reduction table is formed which, together with a reduction algorithm, allows one to arrive at the minimal equivalent machine whenever such a complete reduction is uniquely possible. We do not consider in this paper aspect (*c*) of the synthesis problem which calls for the realization of the reduced machine in terms of hardware.

The formalism is developed such that the various steps in the synthesis procedure can be readily mechanised or programmed on a computer. This is an essential aspect of the problem in practice, since, without some such mechanical assistance, the synthesis of large, complex sequential machines will be almost impossible.

2. CONVENTIONS

Following the customary practice, we shall assume that the input, output and internal state organs of the machine are binary state devices, and refer to them as flip-flops. Thus, let the sequential machine have n input flip-flops and m output flip-flops. Then there are 2^n possible input states and 2^m possible output states. Call the former set I and index its members $(I_0, I_1, \ldots, I_{2^n-1})$; call the latter set Φ and index its members $(\phi_0, \phi_1, \phi_2, \ldots, \phi_{2^m-1})$.

A k-sequence is a sequence of input states of length k. For a given k, every k sequence can be written as a k-tuple whose components read from left to right constitute the input states in that k-sequence. The 1-sequences are the individual input states.

For each fixed k, the k-tuples are ordered according to the lexicographic ordering of their components. Thus, for each k, the first k-tuple is $(I_0, I_0, \ldots, I_0)$ and the last $(I_{2^n-1}, I_{2^n-1}, \ldots, I_{2^n-1})$. There are 2^n 1-tuples, 2^{2n} 2-tuples and in general, 2^{kn} k-tuples.

The integer N is a given parameter for the problem. N is the maximum length of an input sequence identified by the sequential machine as an event. Hence N is a measure of the finiteness of the memory of the machine.

The set of input sequences of lengths k, for $k = 1, \ldots$ N, has

$$\mathcal{J}(N) = 2^n + 2^{2n} + \ldots + 2^{Nn} = \left(\frac{2^n(2^{nN} - 1)}{2^n - 1}\right)$$

members. Call this set $\mathcal{J}$ and index its members with natural numbers (starting from 1). In each set of k-tuples, the indexing follows the ordering

defined earlier. The k-tuples themselves are ordered according to their lengths, starting with the 1-tuples and ending with the N-tuples.

3. The Specification Problem

(*a*) *Aspect.*—It is assumed that the sequential machine always starts from a distinguished initial internal state denoted by S_0. The required behaviour of the machine is now specified by the assignment of outputs from the set Φ to the elements i of $\mathcal{I}$. Thus, if ϕ_a is assigned to i, it means that starting from the initial internal state S_0, the input sequence i terminates with the machine in the output state ϕ_a.

In addition to the above assignments, certain end conditions will have to be prescribed. This is necessary because it was assumed that the sequential machine could identify k-sequences only for $k \leqslant N$. Hence, for completeness, its behaviour for k-sequences with $k > N$ should be specified. (As we shall see, in practice, it is sufficient to specify for $k = N + 1$ in addition to $k \leqslant N$.) This is done, most naturally, by giving explicit rules which identify k-sequences, for $k > N$, with the elements i of $\mathcal{I}$ in a unique manner.

Several cases will have to be distinguished according as the assignment of outputs is complete or partial.

Case 1.—An output is assigned to every element i of $\mathcal{I}$. This is the case of the 'exhaustive' specification and admits of a complete reduction to a minimal machine uniquely.

Case 2.—Outputs are assigned to some elements of $\mathcal{I}$ and it is specified that the assignment of outputs to the remaining elements of $\mathcal{I}$ are not of consequence (and, hence, can be done arbitrarily). The unassigned sequences are the so-called "Don't-care" sequences, and, clearly, any particular solution will depend upon the way outputs are assigned to the 'Don't-care' sequences. Each such completion of assignment will reduce case 2 to an instance of case 1.

Case 3.—Outputs are assigned to some elements of $\mathcal{I}$ and, in addition, auxiliary constraints are prescribed as holding between the elements of $\mathcal{I}$. These constraints may be of the following type:

(*a*) The elements i and k of $\mathcal{I}$ are *indistinguishable* or *equivalent*. By this is meant the following: The same output is assigned to i and k and, in addition, the subsequent behaviour of the machine is identical in the 2 cases. Under these circumstances, it would be natural to say that i and k refer to the same event.

(*b*) Certain input sequences are forbidden, *i.e.*, either they do not occur as inputs to the machine or, if they do, the machine stops, say.

(*c*) Other specialised constraints, if any.

Clearly cases 1, 2 and 3 are not independent. In particular, the exhaustive specification of case 1 contains implicitly all the information required to partition the elements of $\mathcal{I}$ into equivalence classes as described in case 3 (*a*). In fact, what we shall be concerned with in the rest of the paper is the determination of a *uniform* procedure to accomplish just this. Also it must be pointed out that where indistinguishability relations [as in 3 (*a*)] are known to exist, the end conditions cannot be prescribed arbitrarily, but must be obviously consistent (*see* § 7 below).

4. THE ASSIGNMENT OF INTERNAL STATES

The specification of the required machine behaviour having been given, the crux of the remaining problem in synthesis is the assignment of internal states with their transitions such that the resultant machine is minimal. Minimality implies that no machine with a smaller number of internal states will be able to satisfy *all* the specified requirements of behaviour. This problem is best handled in 2 distinct steps, as follows:

Step 1.—First, a uniform procedure is given for assigning internal states to input sequences, *i.e.*, to elements i of $\mathcal{I}$.

Step 2.—Next, a transition table is formed and a uniform procedure is given for finding the equivalence among the internal states. This results in a table with a minimum number of internal states satisfying the specification.

To begin with, we shall restrict our attention to case 1, *i.e.*, that of the 'exhaustive' specification, and develop the details of steps 1 and 2 for this case. Later, we shall show how these details can be suitably modified so as to reduce cases 2 and 3 to case 1.

5. CASE 1: 'EXHAUSTIVE' SPECIFICATION

Step 1: *Assignment of internal states.*—It is assumed here that an output from the set Φ has been specified to *each* element i of $\mathcal{I}$. Now, to each i a distinct internal state S_{i+1} is assigned, starting with S_1 for the 1-tuple $i = 0$. S_0 is the distinguished initial internal state. Thus, Table I, the assignment table, is formed as shown in Fig. 1.

Since the set has

$$\mathcal{I}(N) = \frac{2^n (2^{nN} - 1)}{2^n - 1}$$

members, Table I will have that many rows.

No.	Input sequences (elements i of $\mathcal{I}$)	Output states	Internal states
1	$i=0$	ϕ_{a_0}	S_1
2	$i=1$	ϕ_{a_1}	S_2
3	$i=2$	ϕ_{a_2}	S_3
.	...	...	...
.	...	...	...
$\mathcal{I}(N)$	$i=\mathcal{I}(N)-1$	$\phi_{a_{\mathcal{I}(N)-1}}$	$S_{\mathcal{I}(N)}$

FIG. 1. Table I: The Assignment Table.

Step 2: *Construction of the transition table.*—Using Table I, we wish now to construct Table II, the transition table. The transition table, as shown in Fig. 2, is in the form of a matrix with 2^n columns and $\mathcal{I}(N)+1$ rows. The columns are named $I_0, I_1, \ldots, I_{2^n-1}$ and correspond to the input states with the same names. Similarly, the rows are named $S_0, S_1, \ldots, S_{\mathcal{I}}$ and correspond to the internal states with the same names. Let the cell located at the intersection of row S_i and column I_j be named (S_i, I_j). Each cell (S_i, I_j) contains two entries—one on the left, called the S-entry, which is the name of an internal state, and one on the right, called a ϕ-entry, which is the name of an output state.

The physical significance of the matrix is as follows: The names of the rows refer to the present internal states and those of the columns to the present input states. The S- and ϕ-entries in the cell (S_i, I_j) give the next internal state—present output state pair associated with the present internal state S_i and the present input state I_j.

Each row of Table I contains the names of one internal state and one output state. Each such pair S-ϕ is entered as an S-ϕ entry in one cell of Table II. To begin with, in the first row (named S_0), the S-ϕ pair corresponding to the 1-tuple j (in Table I) is entered in the cell (S_0, I_j). This is done for $j = 0, 1, \ldots, 2^n - 1$. Any other cell (S_k, I_j) with $k > 1$ and $j = 0, 1, \ldots, 2^n - 1$ is now filled in as follows: In Table I consider the input sequence $i(k)$ which has been assigned the internal state S_k. Form the extended sequence by adding I_j to the extreme right of $i(k)$. Let this input sequence be denoted by $i(k)\,I_j$. Now, fill in the cell (S_k, I_j), the S-ϕ

pair in Table I corresponding to the sequence $i(k)\,I_j$. In case $i(k)$ is itself an N-tuple, $i(k)\,I_j$ will be a $(N+1)$-tuple and, hence, there will be no row corresponding to it in Table I. However, by applying the proper end condition to $i(k)\,I_j$, it will be identified with one of the rows of Table I uniquely. The S-ϕ pair of that row is now used to fill in the cell (S_k, I_j).

S_t \ I_t	I_0		I_1		. . .	I_{2^n-1}	
	S_{t+1}	ϕ_t	S_{t+1}	ϕ_t		S_{t+1}	ϕ_t
S_0					. . .		
S_1					. . .		
.	.	.	.	.	. . .	.	.
.	.	.	.	.	. . .	.	.
.	.	.	.	.	. . .	.	.
$S_{\mathcal{J}(N)}$					. . .		

FIG. 2. Table II: The Transition Table.

The form of Table II shows that it is a transition table. The proof that the transition table so obtained does in fact satisfy the specification given follows directly from the explicit rule of construction of the input sequences which correspond to the internal states which are row names of Table II.

Step 2 (*b*): *Construction of the reduction table.*—Referring to Table II, the internal states which are the names of rows, are assigned superscripts according to the following rules. For definiteness, we shall use the Greek letters (in their alphabetical order) for this purpose.

S_i and S_j have the same superscript if, and only if, the ϕ-entries in those two rows, along corresponding columns, are identical.

A uniform procedure for assigning the superscripts may be given. First partition the set of internal states (which are row names) according to their ϕ-entries in the 0th column and assign superscripts. Next, re-partition these subsets according to their ϕ-entries in the 1st column and assign fresh superscripts to the subsets newly formed and so on till the last column is

reached. The internal states which belong to the same subset, after the completion of this operation, will have been assigned the same superscript.

In the modified Table II the row names are internal states with superscripts. From this modified Table II, the reduction table, Table III, is constructed, as shown in Fig. 3. The reduction table is in the form of a matrix, with the rows corresponding to the next internal states (written down in order, starting with S_1, together with their superscripts) and the columns corresponding to the input states written in order from left to right. In the cells are written down those internal states (with their superscripts) which associated with the input state which is their column name give rise to the next internal state which is their row name.

S_{t+1} \ I_t	I_0	I_1	. . .	I_{2^n-1}
	S_t	S_t		S_t
S_1^{α}			. . .	
S_2^{γ}			. . .	
.	.	.	. . .	
.	.	.	. . .	
$S^{\rho_{\mathcal{J}(N)}}$			. . .	

FIG. 3. Table III: The Reduction Table.

This can be done with the help of the modified Table II as follows: write down in cell (S_i, I_j) of Table III all the row names of Table II whose S-entry in the column named I_j is S_i.

In the reduction process, we wish to merge all internal states which are equivalent to one another, into a single state. Thus when the reduction process is complete, we shall be left with a machine with a minimum number of internal states satisfying the specification.

Clearly, the states $(S_{a_1}, S_{a_2}, \ldots, S_{a_n})$ are equivalent if, and only if, they satisfy the 2 conditions:

(1) For every fixed input state I_j, the pair $(S_{a_i} - I_j)$ results in the same output state for all a_i, $i = 1, 2, \ldots, n$.

(2) For every fixed input state I_j, the pairs $(S_{a_i} - I_j)$ result in the next internal states S_{b_i} such that, either all the S_{b_i} are the same, or are equivalent.

From the way the superscripts have been assigned it is evident that, to begin with, in Table III, all internal states satisfying condition 1 will have the same superscripts. However, in general, such states with the same superscripts will not satisfy condition 2. The iteration procedure outlined below will enable us to modify the superscripts systematically, thus, completing the reduction process.

In Table III, let the columns be ordered from left to right and in each column, the cells from top to bottom. We shall say a row has superscript α if the rowname is a next internal state with superscript α.

The modification in the superscripts is done by the addition to them of indices i which are natural numbers. Thus, a re-partitioning of the set with superscript α_i is done by introducing the superscript α_{i+1}. Similarly for β, γ, etc. The superscripts are ordered according to the following scheme:

$$\alpha, \alpha_1, \alpha_2, \ldots\ldots\ldots, \beta, \beta_1, \beta_2, \ldots\ldots, \gamma, \gamma_1, \ldots\ldots$$

As each new superscript is introduced, it is added at once to this list of superscripts at its proper place.

The following iteration scheme is now used:

(A) Find the first cell in column 0 containing an internal state with superscript α. Let its row have the superscript ω. Find the next cell in the same column with an internal state also with the superscript α but whose row has a superscript different from ω, say ω_1. Change all the superscripts α in that cell, and in all the succeeding cells, in the same column, whose rows have superscripts ω_1, to α_{i+1} (where α up to α_i are already in the list of superscripts). Make corresponding changes in the superscripts of these internal states wherever they occur in Table III (including the names of rows). If no such next cell is found, of course, no modification is to be done. Repeat, now, the process with column 1, then with column 2 and so on up to column $2^n - 1$.

Let A be called a minor cycle.

(B) The minor cycle is repeated using α_1 in place of α and, when this is done, with the next superscript in the list in place of the previous one and so on till the entire list of superscripts is exhausted. Let A and B together be called a major cycle.

(C) The major cycle is iterated till no modification of superscripts takes place in one complete major cycle.

The reduction process is now complete and the internal states having the same superscripts are equivalent and hence can be merged.

The proof that this iteration procedure terminates and does result in complete reduction of the equivalent states is straightforward and we shall not go into the details here. In fact, the procedure given above is essentially a systematization of Mealy's Rule I [pp. 1056 of (4)].

6. Case 2: Specification with 'Don't-Care' Sequences

Here, outputs are specified for some elements i of $\mathcal{I}$ and the remaining elements of $\mathcal{I}$ are specified as 'dont'-care' input sequences. Table I is now constructed, as before, assigning a distinct internal state S_{i+1} to each input sequence i. The ϕ-entries for the 'don't-care' sequences are written in as D.

Thus, when Table II is constructed from Table I, some of the cells will contain D as their ϕ-entries. Before forming the modified Table II, each entry marked D will have to be replaced by a particular ϕ_k. Superscripts are now assigned to the rownames and the reduction process completed as before. Clearly, every such replacement of the D's by the ϕ's will result in a reduced machine satisfying the given specification.

The problem of great interest, in practice, is how to assign the ϕ_k's to the D's so that the reduced machine has a minimum number of internal states. Clearly, not much can be said about this in detail, since the solution for any specific case will depend on the way the D's are distributed among the cells of Table II. However, in general, the aim should be to assign the ϕ_k's so as to minimise the number of distinct superscripts in the modified Table II.

7. Case 3: Specification with 'Input Equivalences'

In this case, outputs are specified to certain elements of $\mathcal{I}$ and, in addition, certain input sequences are specified as equivalent or indistinguishable (in the sense described in § 3), and certain other input sequences are forbidden. There may or may not be 'don't-care' sequences, besides.

It is to be pointed out here that if sequences i and k are equivalent, then for all j, $0 \leqslant j \leqslant 2^n - 1$, the extended sequences $i\mathrm{I}_j$ and $k\mathrm{I}_j$ will have to be equivalent.

In forming Table I, the outputs are written in wherever they are specified and they are marked D for the 'don't-care' sequences, if any. Distinct internal states are now assigned, in order, starting from S_1 for the input sequence $i = 0$. All the input sequences specified as equivalent are assigned the same internal state. The forbidden sequences are assigned the internal state F. Thus, if sequence i has been assigned the internal state S_k and if

j is the next sequence (in Table I) which is not equivalent to any l for $l < j$, then j is assigned the internal state S_{k+1}.

Let M be the total number of distinct internal states assigned in making up Table I. Table II is now formed with $(M + 2)$ rows and 2^n columns. The columns refer to the input states, as usual, while the rows are named to correspond to the internal states, without any repetition. The first row is named S_0, the ith row, for $2 \leqslant i \leqslant M + 1$ is named S_{i-1} and the last row is named F.

The cells in the row S_0 are filled in as before. The cell (S_k, I_j), for $1 \leqslant k \leqslant M$ is filled in as follows: Let $i(k)$ be the *smallest* input sequence in Table I which has been assigned the internal state S_k. Form the input sequence $i(k)\ I_j$ by adding I_j on the extreme right of $i(k)$. Now, fill in the cell (S_k, I_j), the $S - \phi$ pair corresponding to the sequence $i(k)\ I_j$ in Table I. In case $i(k)\ I_j$ happens to be a $(N + 1)$-tuple, it has to be reduced to a 1-tuple, for $l \leqslant N$, with the help of the given end conditions before applying the above rule.

All the cells in the last row named F have F as their S-entry and ϕ_F as their ϕ-entry, where ϕ_F is the output specified for any forbidden sequence. (Note that all forbidden sequences are equivalent.)

It is a straightforward process to verify that the transition table so constructed is complete and consistent, in the sense that every input sequence i occurring in Table I can be built out of Table II starting with S_0 and that it will terminate in the same internal state S (i) as that specified for i in Table I.

Case 3 is now reduced to case 1 and the rest of the reduction process will go through as outlined in § 6 if there are ' don't-care ' sequences, or else as in § 5.

8. CONCLUDING REMARKS

In this paper we have been mainly concerned with the synthesis of sequential machines given their required behaviour in terms of events and associated outputs. The emphasis has been on obtaining a uniform procedure, the details of which can be programmed on a computer with ease. Although the formalism developed here is complete as far as it goes, it should be pointed out that several problems remain open. Here, we shall refer to only two which bear directly on the contents of this paper.

The first is concerned with the problem of specification. Although it follows from Kleene's results that everything that any finite automaton does can be completely described in terms of events and outputs, this does not, in practice, seem to be of much help. Presumably, there are behaviours

which are intuitively meaningful but which one does not know how to express in terms of events and outputs. It should be useful to have a uniform procedure for doing this, if not in every case, at least, in a suitably well-defined large class of cases.

The second problem has to do with the design of complex sequential machines. In practice, one tries to visualise a large machine as made up of submachines, each functionally independent to a large extent, and thus reduce the given problem to one of synthesising a large number of smaller machines. In such cases, there may be feedback loops from the output of one submachine to the input of another and problems analogous to those of ' stability ' might arise. It might be useful to consider modifications or suitable extensions of the formalism given here to include these cases.

That both these problems are of great practical importance is shown by the fact that they play a central role in the specification and design of large-scale digital computers. It is of interest to note that digital computers, although seemingly well understood from the point of view of their description as sequential machines, still fall outside the scope of all existing *routine* synthesis procedures, for the most part.

9. Illustrative Examples

In this final section, we give two examples illustrating the concepts and the methods introduced in the paper.

Example 1.—Synthesis of a sequential machine with one input flip-flop and two output flip-flops and whose output is a function of utmost the three previous inputs. The required behaviour is specified exhaustively by means of the assignment table in Fig. 4. (The 2 input states are denoted as 0 and 1 and the 4 output states by 00, 01, 10 and 11 respectively.)

End condition.—If $I_1I_2 \ldots I_{k-2}I_{k-1}I_k$ is any sequence of length k, for $k \geqslant 3$, then, it is equivalent to the sequence $I_{k-2}I_{k-1}I_k$.

From Fig. 4, one obtains the modified transition table as shown in Fig. 5. The reduction table, at the end of complete reduction, is shown in Fig. 6. Thus, the equivalent states are:

α: (S_0);
α_1: (S_1);
α_2: $(S_4, S_6, S_8, S_{10}, S_{12}, S_{14})$;
β: (S_2);
β_1: (S_3, S_7, S_{11});
γ: (S_5, S_9, S_{13}).

No.	$\mathcal{J}$	ϕ	S
1	0	00	S_1
2	1	01	S_2
3	00	00	S_3
4	01	01	S_4
5	10	01	S_5
6	11	10	S_6
7	000	01	S_7
8	001	11	S_8
9	010	00	S_9
10	011	01	S_{10}
11	100	10	S_{11}
12	101	10	S_{12}
13	110	00	S_{13}
14	111	01	S_{14}

FIG. 4. The Assignment Table.

S_t \ I_t	0		1	
	S_{t+1}	ϕ_t	S_{t+1}	ϕ_t
$S_0{}^{\alpha}$	S_1	00	S_2	01
$S_1{}^{\alpha}$	S_3	00	S_4	01
$S_2{}^{\beta}$	S_5	01	S_6	10
$S_3{}^{\beta_1}$	S_7	01	S_8	11
$S_4{}^{\alpha}$	S_9	00	S_{10}	01
$S_5{}^{\gamma}$	S_{11}	10	S_{12}	10
$S_6{}^{\alpha}$	S_{13}	00	S_{14}	01
$S_7{}^{\beta_1}$	S_7	01	S_8	11
$S_8{}^{\alpha}$	S_9	00	S_{10}	01
$S_9{}^{\gamma}$	S_{11}	10	S_{12}	10
$S_{10}{}^{\alpha}$	S_{13}	00	S_{14}	01
$S_{11}{}^{\beta_1}$	S_7	01	S_8	11
$S_{12}{}^{\alpha}$	S_9	00	S_{10}	01
$S_{13}{}^{\gamma}$	S_{11}	10	S_{12}	10
$S_{14}{}^{\alpha}$	S_{13}	00	S_{14}	01

FIG. 5. The Modified Transition Table.

In Fig. 7 is given the state diagram of the completely reduced machine. It is easily seen that this diagram is not further reducible.

Example 2.—We give here, in terms of our notation, the specification for the ' reversible counter ' considered by Huffman [pp. 276 of (2)].

S_{i+1} \ I_i	0	1
	S_i	S_i
$S_1^{\alpha_1}$	S_0^{α}	
S_2^{β}		S_0^{α}
$S_3^{\beta_1}$	$S_1^{\alpha_1}$	
$S_4^{\alpha_2}$		$S_1^{\alpha_1}$
S_5^{γ}	S_2^{β}	
$S_6^{\alpha_2}$		S_2^{β}
$S_7^{\beta_1}$	$S_3^{\beta_1}$, $S_7^{\beta_1}$, $S_{11}^{\beta_1}$	
$S_8^{\alpha_2}$		$S_3^{\beta_1}$, $S_7^{\beta_1}$, $S_{11}^{\beta_1}$
S_9^{γ}	$S_4^{\alpha_2}$, $S_8^{\alpha_2}$, $S_{12}^{\alpha_2}$	
$S_{10}^{\alpha_2}$		$S_4^{\alpha_2}$, $S_8^{\alpha_2}$, $S_{12}^{\alpha_2}$
$S_{11}^{\beta_1}$	S_5^{γ}, S_9^{γ}, S_{13}^{γ}	
$S_{12}^{\alpha_2}$		S_5^{γ}, S_9^{γ}, S_{13}^{γ}
S_{13}^{γ}	$S_6^{\alpha_2}$, $S_{10}^{\alpha_2}$, $S_{14}^{\alpha_2}$	
$S_{14}^{\alpha_2}$		$S_6^{\alpha_2}$, $S_{10}^{\alpha_2}$, $S_{14}^{\alpha_2}$

FIG. 6. The Reduced Table.

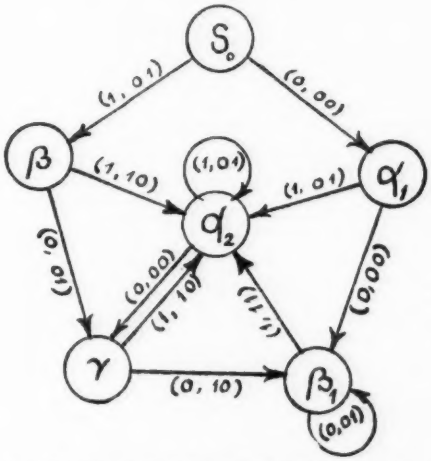

FIG. 7. The State Diagram of the Minimal Machine.

4 input states: I_0, I_1, I_2, I_3

4 ouput states: $\phi_0, \phi_1, \phi_2, \phi_3$

Restraints on input sequences:

(1) For any I_j, $I_0 I_j = I_j I_0 = I_j$.

(2) I_3 is forbidden.

Output assignments:

(1) I_0 has the output ϕ_0.

(2) If i is any sequence with output ϕ_{a_i}.

Then iI_1 has output $\phi_{a_{i+1}}$ (Mod. 4).

iI_2 has output $\phi_{a_{i+3}}$ (Mod. 4).

iI_0 has output ϕ_{a_i}

It is easily verified that, with the above, the assignment table can be completely filled in and the reduction process carried through.

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